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PRELIMINARY REPORT

ON THE THERMODYNAMIC PROPERTIES OF

SELECTED LIGHT-ELEMENT AND

SOME RELATED COMPOUNDS

(The previous semiannual reports in this series have the NBS Report Nos. 6297, 6484, 6645, 6928, 7093, 7192, 7437, 7587, 7796, 8033, 8186, 8504, 8628, 8919, 9028, 9389, 9500, and 9601.)

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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Technical Summary Report
on the Thermodynamic Properties
of Light–Element Compounds

Reference: U. S. Air Force, Office of Scientific Research,
Order No. ISSA 67–6

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ABSTRACT

Thermodynamic and related properties of substances important in current high-temperature research and development activities are being investigated under contract with the U. S. Air Force Office of Scientific Research (USAF Order No. ISSA 67-6) and the Advanced Research Projects Agency (ARPA Order No. 20). This research program is a direct contribution to the Interagency Chemical Rocket Propulsion Group (Working Group on Thermochemistry) and, simultaneously, to other organizations oriented toward acquiring the basic information needed to solve not only the technical problems in propulsion but also those associated with ballistics, reentry, and high-strength high-temperature materials. For given substances this needed basic information comprises an ensemble of closely related properties being determined by an extensive array of techniques. Some of these techniques, by relating thermodynamic properties to molecular or crystal structure, make it possible to tabulate these properties over far wider ranges of temperature and pressure than those actually employed in the basic investigations.

This report presents the results and interpretation of five recent NBS experimental studies of thermodynamic properties, two reviews which refine data treatment and evaluation, and one new critical assessment of published heats of formation. The heat capacity of beryllium nitride, Be_3N_2, was precisely measured from 0 to 315 K; after judicious correction for the irreducible impurities, the data led to the common thermodynamic properties from 0 to 315 K, complementing earlier NBS measurements from 273 to 1173 K. Precise high-temperature calorimetry gave the heat capacity of tungsten from 1100 to 2600 K (showing no detectable difference between two samples, one triple-zone-refined and 99.999% pure); finally corrected results are given also for solid and liquid beryllium aluminate, $BeAl_2O_4$, from 1200 to 2400 K. A mass-spectrometric investigation of Al_2O_3 containing 5.8% BeO identified the high-temperature gas species and gave values for their standard

heats of formation. As part of the current NBS microwave and infrared investigation of the alkali-hydroxide molecules, the high-temperature microwave spectra of four isotopic varieties of RbOH were observed and analyzed to give their molecular constants; like CsOH (studied earlier), RbOH is linear, with a low-frequency bending vibration of large amplitude. Two reviews deal with reaction calorimetry involving fluorine compounds: One documents the inadequacy of estimation rules for unmeasured inorganic fluorides, and recommends a systematic cataloging of results to achieve better consistency; while the other describes a new computer subroutine for the automatic reduction of bomb-calorimetry data on organic fluorine compounds. As the result of an up-to-date critical evaluation of the published data giving ΔHf°_{298}, ΔGf°_{298}, and S°_{298} of magnesium compounds, values are documented and tabulated for 60 species of interest in "light-element" applications.

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Chapter 1

THE THERMOCHEMISTRY OF INORGANIC FLUORINE COMPOUNDS THE NEED FOR A CATALOG OF THERMOCHEMICAL PROCESSES[1]

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1. ESTIMATES OF HEATS OF FORMATION

Some years ago we reviewed (see for example [1]) the effectiveness of estimates of the heats of formation of inorganic fluorine compounds by a procedure which we have not seen used elsewhere. We compared estimates of heats of formation for which no measured value existed at the time of the estimate, with later values measured experimentally. The estimates were, thus, a priori in a sense. By this tactic we hoped to avoid the possibility of (no doubt unpremeditated) influence of the measured value upon the quality of the estimate. We considered, for instance, that if a measured value were available the author of an estimate might be influenced favorably in his decision to publish by good agreement of his estimate; or, contrariwise, unfavorably and decide not to publish if agreement were poor; thus we would anticipate that estimates made after the availability of experimental data might tend to be better than estimates made prior to such availability.

Some new information has been added and the comparisons are shown in Table 1. The average error (without regard to sign) is 44 kcal mol^{-1}, and the average bias is 26 kcal mol^{-1} positive, as compared with our earlier finding of 30 and 17 kcal mol^{-1}, respectively. Thus, the ability to estimate heats of formation was not particularly good, and recent data have continued to show large deviations. The tendency is for the compounds of fluorine to be more stable than estimated.

The difficulty may be due in part to the extreme position of fluorine in the periodic system, which causes all attempts to estimate on the basis of the properties of neighboring elements to be extrapolations rather than interpolations.

[1] Prepared for presentation at the Thermodynamic Symposium of the IUPAC Commission on Thermodynamics and Thermochemistry, Heidelberg, West Germany, September 1967.

Table 1

Accuracy of Estimates of Heats of Formation of Some Fluorine Compounds

Compound	ΔH_f kcal mol^{-1}		Error
	Estimate	Later Measurement	
$AcF_3(c)$	-420	-477	+57
	-395		+82
$AlF_3(c)$	-311	-361.0	+50
	-323		+38
$AuF_3(c)$	-100	- 83.3	-17
$BeF_2(c)$	-227	-245.3	+18
	-220		+25
$HfF_4(c)$	-435	-461.4	+26
$MoF_6(\ell)$	-405	-388.6	-16
$NF_2(g)$	17	8.9	+ 8
$NbF_5(c)$	-342	-432	+90
$PF_5(g)$	-315	-381.4	+66
	-420		-39
$RuF_5(c)$	-300	-213.4	-87
$SF_4(g)$	-156	-171.7	+16
$TaF_5(c)$	-300	-455	+155
	-360		+95
$ThF_4(c)$	-477	-482	+ 5
$TiF_4(c)$	-370	-394.2	+24
$TlF(c)$	- 65	- 74.0	+ 9
$TlF_3(c)$	-175	-136.9	-38
$ZrF_4(c)$	-445	-456.8	+12

Average error 44 kcal mol^{-1}

Average bias 26 kcal mol^{-1}

Estimates are selected from a review by Armstrong and Krieger [2].

We have not made a general study of the problem of predictions of binding energies or of the relative effectiveness of the different methods that have been used. This is a worthwhile exercise, and possibly if we had done so we would have somewhat less of a blunderbuss approach to the results. However, our concerns up to now at least have been primarily in other directions. The information which has been presented to you was enough to persuade us to adopt a skeptical attitude toward estimates. It is apparent that competent and well established reviewers have on the whole shown a lack of ability to predict a priori with reasonable accuracy the heats of formation of inorganic fluorine compounds.

2. SOME SOURCES OF EXPERIMENTAL DIFFICULTY IN MEASUREMENTS

The unusual bias of predictions, together with a curious regularity observed in successive experimental determinations of certain heats of formation, led to the formulation of a rather general rule, that members of our laboratory have rather facetiously termed Armstrong's rule: as time goes by heats of formation tend to become more negative. In the denouement we hold no brief for this rule, but point it out as an interesting interlude in our examination of the findings of experimental thermochemistry.

An example that led to this attitude is the heat of formation of aluminum oxide (Table 2) which became significantly more negative over a period of 30 years. The heat of formation of AlF_3 has followed roughly this rule, we see semblences of it also in the heats of formation of BeO(c), BeF_2(c), CF_4(g), and HF(aq).

Table 2

Successive Determinations $\Delta H_f[Al_2O_3(c,\alpha)]$

	kcal mol^{-1}
Moose and Parr (1924) [3]	-376.9
Roth and Muller (1929) [4]	-380.1
Snyder and Seltz (1945) [5]	-399.09
Oketani and Maebashi (1950) [6]	-381.03
Holley and Huber (1951) [7]	-400.29
Schneider and Gattow (1954) [8]	-400.6 (-402)[a]
Mah (1957) [9]	-400.4

[a] The number in parenthesis included a questionable correction made by the authors for partial formation of a less stable phase.

When we examine these tendencies in greater detail, however, we find, perhaps not surprisingly, that the picture was oversimplified. Still, certain regularities of behavior do persist, and lead us to believe there is some rational explanation of these regularities. The explanations which finally appear to emerge are not the same in every case. That is, a variety of influences is apparently at work. An examination of a few of them may assist us in planning future experimental work.

We return to the heat of formation of Al_2O_3 briefly and note that each value quoted resulted from combustion of the metal in oxygen. With a little imagination we realize that probably the cause of progressively more negative heats of formation was better control of the amount of reaction as time passed. The less negative values probably represent smaller amounts of reaction than the experimenter presumed. There may be two reasons for this bias: (1) the sample metal may have contained larger amounts of inert impurities than were revealed by analysis; (2) the metal may have reacted less completely than presumed. The first source of error is rendered plausible by the finding of relatively large amounts of oxygen and nitrogen (probably as a surface coating) in metals even supposedly highly pure on the basis of spectrographic analysis. The second source of error is rendered plausible by the fact that the combustion product may completely cover small amounts of unburned metal and preclude further oxidation. On the basis of an argument like the above, we would anticipate in the combustion of refractory substances giving solid products, a bias in the direction of low heat of reaction which might be substantial in some cases. A notorious example of this is the combustion of boron in oxygen, for which the two processes may both be presumed to be severe. Let us turn to a more complicated and informative example, the heats of formation of CF_4 and HF.

A few years ago, apparently valid but inconsistent experiments were reported by Jessup [10] on the one hand and by Good, Scott and Waddington [11] and by Neugebauer and Margrave [12] on the other hand, all of which gave values for the heat of formation of CF_4. See Table 3. In an attempt to reconcile them we observed the opposing sense in which the heat of formation of HF occurred in the relationships between the heats of reaction and the heat of formation of CF_4. These relationships are shown in Table 4, referring to reactions 2, 3b, and 4c. This led us to make the

suggestion that possibly the heat of formation used for HF in the calculation was in error, and it was no problem then to figure a reasonable change in the heat of formation of HF that would reconcile these inconsistent sets of experiments.

In Table 3 we list all the reactions involving CF_4 for which we have found calorimetric studies.

If we restrict ourselves to the reactions from which the heat of formation of CF_4 is derived by its difference from HF (rather than from its sum with HF) as in reactions 3(a,b,d), 4(a,b,c), 5(a,b,c) and possibly 8, and 9, we find a rather nice consistency between the calculated values for CF_4 no matter what value is selected for HF(aq). An illustration of this is given by Cox, Gundry, and Head [13], using an extreme value for the heat of formation of HF(aq).

The heat of formation of CF_4 as inferred from these experiments is inextricably bound to the heat of formation of HF(aq). It is evident that we shall not learn anything further about it from them alone, so long as there is fluctuating information about the heat of formation of HF.

We may turn to the experiments that do not involve HF. Here we find ourselves in reaction sets 1, 6, and possibly 8 and 9, immediately faced with the same problems or at least similar problems to that mentioned earlier in the case of Al_2O_3. For instance, in reactions (8) and (9), involving the reduction of an organic compound and the formation of a solid residue carbon, the question arises, "to what extent has this reaction gone to completion?" Completion here includes two concepts: (1) has all of the F been extricated from the C residue? and (2) has the C residue been reduced to a recognizable, well defined standard state, or does it retain active centers (as a result of a large surface area, for example)? The experimental evidence, particularly with respect to the latter problem, as outlined in the notes to Table 1 is disheartenningly unsatisfactory. One is left with the feeling that the observed heat processes will tend to be biased toward the low side of the true heat of reaction.

Only by the most careful experimentation can one be sure that the observed heat actually corresponds to the expectation for a complete reaction described exactly by the equation.

Somewhat peripheral to our subject, the analysis of these equations led us to an understanding:

(1) That the heat of formation of CF_4 is best represented by the experiments on direct combustion of graphite in fluorine; and by a combination of the combustion of "Teflon" in oxygen and in fluorine, the only products being gaseous CO_2 and CF_4.

(2) That other reactions not involving HF do not provide any conflicting evidence, but that the positive information they provide is limited by the lack of characterization of the reaction.

(3) That reactions involving HF(aq) do not provide conflicting evidence, but that the positive information they supply is limited by uncertainty in the heat of formation of HF(aq). (Incidentally, tne reaction by Jessup et al. [10] which was an initiator of the line of thought described here, turns out now to be inconsistent in the opposite sense from what it was at the outset, and no means of reconciliation is now apparent.).

(4) That the reactions involving HF(aq) can be combined with independently arrived at values for heats of formation of CF_4 as well as BF_3 and NF_3) to arrive at new "consensus" values for the heat of formation of HF(aq). Figure 1 shows the apparently most consistent value for heat of formation of HF(aq).

(5) That the explanation of the observed discrepancies in measurements of the heat of formation of HF(g) or HF(aq) by various means may involve subtle arguments. The large deviation of the work of Cox and Harrop [19], for instance, may be due not to experimental error but to a residual entropy of $LiHF_2$(c) at absolute zero, or to use of an inappropriate value for the heat of formation of gaseous HF. In the latter event, the heat of formation of gaseous HF is still a problem.

3. CATALOGING THE CALORIMETRIC PROCESSES

A feature is present in Table 1 which, undoubtedly, is not new but suggests to us what we believe is a new concept of the appropriate forms for presenting calorimetric (and other thermodynamic) data.

We have no question in our mind that the most useful form of thermodynamic information for the general user — the theoretician interested in energies of substances, and the engineer interested in design parameters — is a set of tables of values of thermal functions of the substances in the style of NBS Circular 500 [20] (now Technical Note 270-1) [21] or of the JANAF Thermochemical Tables [22] from the U.S.A. or the Thermal Constants of Substances [23] and Thermodynamic Properties of Individual Substances [24] from the Academy of Sciences of the USSR. However, for the thermochemist, the experimental calorimetrist, or the selector of best values, another form seems at least as desirable, and in the latter case almost a necessary adjunct to his work. This form is a catalog of thermochemical processes.

We have seen in Section 2 that a set of equations together with the heat values associated with them is a flexible tool for attempting to determine true values of the heats of formation, and to appraise sources of errors. It is also apparent that critical substances for further study would be discernible in such a set of equations.

A catalog can be conceived of as a tabulation of observed processes — chemical reactions, phase changes, and so on — listed as equations, with the value of the thermal effect observed. Limited amounts of selected information concerning the conditions of the experiment are also included. The tabulation of equations is indexed with respect to all substances and phases present, so that all processes involving a given substance can be located.

The limited list of equations involving CF_4 given in Table 3 represents a skeleton of a limited segment of such a catalog. To prepare a complete catalog including all the chemical substances for which measurements have been made is a very large task. In the following paragraphs we indicate certain special features of such a compilation and suggest the long term benefits which it might be expected to provide.

There is ample evidence that several groups now have essentially the framework of such a catalog. These are the groups which have been for some years compiling and critically evaluating thermodynamic data. The awkward feature of the present situation is that the information, except for the end result after it has been critically evaluated and released in tables of selected values, is essentially in the form of private files. In this form it is inaccessible to the general investigator; in the event of the

formation of a new critical evaluation group, they must acquire their own file of such working information; in the event of the demise of one of these groups, its literature files would probably revert to inutility.

We suggest that much of the intermediate information gleaned from the thermochemical literature is of permanent value, subject to reuse in various ways, and susceptible to augmentation as time goes on without loss of any of the original body of information. In this respect, particularly it is more useful than a collection of selected values of thermodynamic functions, whose values change as new data are added.

A catalog in the form described can be looked upon as a set of mathematical equations or expressions of which a selection is given in Table 4. In general, most of the thermodynamic relationships involving heats of formation can be described as linear equations. The set of possible chemical reactions involving all the chemical substances may be looked upon as a set of simultaneous equations. Experimental enthalpy changes can be expressed in terms of the numerical coefficients and heats of formation of the substances present.

Because of the complexity and number of these equations, and the difficulty of finding simultaneous solutions which offer the best values of the heats of formation, the practice has been adopted of evaluating heats of formation sequentially, starting with certain "key" substances, to which values of heat of formation are assigned on the basis of carefully selected equations.

In principle, if the experimental enthalpy equations are known for any given set of substances, a set of best values can be selected which minimizes the ensemble of errors without predetermining any one key substance. This minimization is ordinarily not done because of its difficulty.

It is to be presumed that the use of high speed computers will ultimately allow selections of best values in this sense for the whole body of chemical substances for which data exist. A catalog of the type described above is a critical development if such a calculation is to be achieved. The catalog will essentially provide the input data for such a selection of best values.

With a workable program for making such selections, it should be possible to make selected best values annually, or more frequently; it should be possible to study the relative importances of various substances; and also to find those substances whose present values appear to be out of line and require redetermination.

Thus a catalog provides three services:

(1) A resource for experimental calorimetrists for planning their work.

(2) Source material for groups preparing best values of thermodynamic properties.

(3) Input data for computerized selection of best values and other computerized analysis of data.

References to the General Text

[1] G. T. Armstrong, J. Chem. Ed. 41, 297-307 (1964).

[2] G. T. Armstrong and L. A. Krieger, in "Progress in International Research on Thermodynamic and Transport Properties," J. F. Masi and D. H. Tsai, Editors, (Academic Press, N. Y. 1962), pp. 8-78.

[3] J. E. Moose and S. W. Parr, J. Am. Chem. Soc. 46, 2656-61 (1924).

[4] W. A. Roth and D. Muller, Z. Physik. Chem. (Leipzig), A144, 253-8, (1929).

[5] P. E. Snyder and H. Seltz, J. Am. Chem. Soc. 67, 683-5 (1945).

[6] S. Oketani and Y. Maebashi, J. Japan. Inst. Metals 14B, No. 2, 27-31, (1950).

[7] C. E. Holley, Jr. and E. J. Huber, Jr., J. Am. Chem. Soc. 73, 5577-9, (1951).

[8] A. Schneider and G. Gattow, Z. Anorg. u. Allgem. Chem. 277, 41-8, (1954).

[9] A. D. Mah, J. Phys. Chem. 61, 1572-3 (1957).

[10] R. S. Jessup, R. E. McCoskey, and R. A. Nelson, J. Am. Chem. Soc. 77, 244-5 (1955).

[11] W. D. Good, D. W. Scott, and G. Waddington, J. Phys. Chem. 60, 1080-9 (1956).

[12] C. A. Neugebauer and J. L. Margrave, J. Phys. Chem. 60, 1318-21 (1956).

[13] J. D. Cox, H. A. Gundry, and A. J. Head, Trans. Faraday Soc. 60, 653-65 (1964).

[14] E. S. Domalski and G. T. Armstrong, J. Res. Nat. Bur. Std. 71A (1967) (In press).

[15] G. K. Johnson, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. 70, 1-6 (1966).

[16] G. H. Sinke, J. Phys. Chem. 71, 359 (1967).

[17] E. S. Domalski and G. T. Armstrong, J. Res. Nat. Bur. Std 71A, 105-18 (1967).

[18] R. C. King and G. T. Armstrong, Unpublished data.

[19] J. D. Cox and D. Harrop, Trans. Faraday Soc. 61, 1328-37 (1965).

[20] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Std. (U.S.), Circ. 500, (U. S. Government Printing Office, Washington, D. C., 1952, 1961).

[21] D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, National Bureau of Standards Technical Note 270-1, (U.S. Government Printing Office, Washington, D. C., 1965).

[22] JANAF Thermochemical Tables, Dow Chemical Company, Midland, Michigan (1960-67).

[23] V. P. Glushko, et al., Thermal Constants of Substances (Akad. Nauk SSSR, Moskva 1965, 1966).

[24] V. P. Glushko, et al. "Thermodynamic Properties of Individual Substances (Akad. Nauk SSSR, Moskva 1962).

Table 3. Thermochemical Studies Involving Tetrafluoromethane

	Reaction	ΔH^{o}_{298} Kcal mol^{-1}	References*
1.	$C(c,graphite) + 2F_2(g) = CF_4(g)$	-162 ± 2[a]	[1]
		(-183.5 ± 2)[b]	[3]
		-222.87 ± 0.38	[6]
2.	$CH_4(g) + 4F_2(g) = CF_4(g) + 4HF(g)$	-459.3 ± 9	[7]
3(a)	$C_2F_4(g) = CF_4(g) + C(c,graphite)$	-61.43 ± 1.4	[8]
		-65.4 ± 0.42	[9]
(b)	$C_2F_4(g) + 2H_2(g) + 4[118.2H_2O](\ell) = 4[HF+118.2H_2O](\ell) + 2C(c,graphite)$	-150.8 ± 1.1	[9]
(c)	$C_2F_4(g)+2H_2(g) = 4HF(\ell)+2C(c,graphite)$	-132.72 ± 0.7	[8]
(d)	$4[HF+118.2H_2O](\ell) + C(c,graphite) = CF_4(g)+2H_2(g) + 4[118.2H_2O](\ell)$	$+85.4\pm1.5$	
(e)	$4HF(\ell)+C(c,graphite) = CF_4(g) + 2H_2(g)$	$+67.32$	
4(a)	$C_2F_4(solid\ polymer)+O_2(g) = CO_2(g)+CF_4(g)$	-118.8 ± 0.5	[10,11]
(b)	$C_2F_4(solid\ polymer)+O_2(g) + 42H_2O(\ell) = 2CO_2(g)+4[HF+10H_2O](\ell)$	-160.3 ± 0.9	[10,11]
(c)	$CO_2(g)+4[HF+10H_2O](\ell) = CF_4(g)+42H_2O(\ell)$	$+41.5\pm1.0$	[10,11]
5(a)	$C_{12}F_{22}(\ell)+6.5O_2(g)+401.8H_2O(\ell) = 0.6CF_4(g) + 11.4\ CO_2(g) + 19.6[HF+20H_2O](\ell)$	$-4067.9/4.184$	[12]
(b)	$C_{12}F_{22}(\ell)+6.5O_2(g)+131.2H_2O(\ell) = 3.9CF_4(g) + 8.1CO_2(g) + 6.4[HF+20H_2O](\ell)$	$-3496.5/4.184$	
(c)	$CO_2(g)+4[HF+20H_2O](\ell) = CF_4(g)+82H_2O(\ell)$	$+41.38\pm0.32$	[12]
6(a)	$C_2F_4(solid\ polymer)+F_2(g) = 2CF_4(g)$	$-247.85(-247.43)\pm0.30$	[5,6]
		-246.84 ± 0.07	[17]
(b)	$C_2F_4(solid\ polymer)+O_2(g) = CO_2(g)+CF_4(g)$	-118.8	[10,11]
(c)	$CO_2(g) + F_2(g) = O_2(g) + CF_4(g)$	$-129.05(128.63)$	
7.	H_2, O_2, CO, CF_4	-220.1 ± 1.4	[13]
8.	$CF_4(g)+4K(c) = 4KF(c) + C(graphite)$	-307 ± 4	[2,4]
		-320 ± 2	[15]
9.	$CF_4(g)+4Na(c) = 4NaF(c)+C(graphite)$	-325.5 ± 2.2	[16]

*See separate set of references for Table 3.

Notes to Table 3

1. a. The original authors made an adjustment of 2.4 kcal mol^{-1} for the estimated heat of formation of the Norite (activated wood charcoal) they burned. They obtained -165.0 ±1.5 kcal mol^{-1} for the combustion of Norite in fluorine. When adjusted by +2.4 kcal mol^{-1} this gives -162.6 kcal mol^{-1} which they apparently rounded to -162 kcal mol^{-1}, increasing the uncertainty to 2 kcal mol^{-1}.

   b. This is an adjustment by Ruff and Bretschneider [3] of the work of von Wartenberg and Schuette [1], taking into account the formation of several percent of higher fluorocarbons in the combustion of Norite. The recalculation changes the original data far too little. A recalculation using a more current value for the fluorination of a C-C bond (142.7 kcal mol^{-1}, instead of 107 kcal mol^{-1} as was used by Ruff and Bretschneider) leads to ΔH_r = -190.5 kcal mol^{-1}. Hence it appears that the formation of other products would have to be greater than was suggested by Ruff and Bretschneider. The uncertainty in amount of products seems to preclude further consideration of the work of von Wartenberg and Schuette.

2. As a part of its uncertainty the work of Jessup, McCoskey, and Nelson [7] contains an uncertain correction of 1.5 to 2.0 kcal mol^{-1} (of CF_4) for nonideality of HF. This now appears to have been an excessive correction. In the extreme case, if this correction is reduced to zero, the heat of reaction becomes -461.2 kcal mol^{-1}. The large uncertainty assigned by the authors is apparently a 95 percent confidence limit.

3. a. The carbon formed in the reaction by Duus [8] was weakly crystalline. Duus made no adjustment to the heat for the physical state of the graphite. An adjustment of the magnitude made by Neugebauer and Margrave [9] would bring Duus' value to -63.3 kcal mol^{-1}. Neugebauer and Margrave [9] measured the heat of reaction, with the formation amorphous carbon, to be -63.5 kcal mol^{-1}, and measured the heat of formation of the amorphous carbon to be 1.9 kcal mol^{-1}. We have combined their measurements to give the heat of decomposition to form graphite, -65.4 kcal mol^{-1}.

b,c. Neugebauer and Margrave [9] measured the heat of hydrogenation of $C_2F_4(g)$, with the formation of HF(aq) and amorphous carbon, to be -147.8 kcal mol^{-1}, and measured the heat of formation of the amorphous carbon to be 3.0 kcal mol^{-1}. We have combined their measurements to give the heat of hydrogenation to form HF(aq) and graphite, ΔH = -150.8 kcal mol^{-1}. Their reaction is definitely superior to reaction 3(c) as carried out by Duus, who was forced to make large corrections for the presence of HF(g), and did not attempt any correction for the physical state of the carbon formed. Neither reaction 3(b) nor 3(c) can be used by themselves to calculate the heat of formation of CF_4, but are included because they can be combined with other work done in the same laboratory to obtain a relationship leading to the desired value.

d. This reaction is obtained by subtracting 3(b) from 3(a). The heat value cited was obtained using the heat of reaction 3(a) determined by Neugebauer and Margrave [9].

e. The heat of this reaction was determined by combining the energy of reaction 3(c) with that for 3(a) determined by Duus [8] and reported in the same paper.

4. a,b. The energies of these reactions were obtained by Good, et al. [10], [11] by extrapolating respectively to x = 1 and x = 0 from measurements covering the range x = 0.0285 to x = 0.8162 of the reactions C_2F_4(solid polymer) + $O_2(g)$ + $4\frac{1}{2}(1-x)H_2O(l)$ = $(2-x)CO_2(g)$ + xCF_4 + $4(1-x)[HF + 10H_2O](l)$. The experiments are carefully described.

c. The heat of this reaction was obtained by combining the heats of reactions 4(a) and 4(b) determined in the same laboratory.

5. a. The heat of this reaction was obtained by Cox, Gundry, and Head [12] by appropriately combining reactions 5(a) and 5(b).

6. a. An earlier (in parentheses) and a more recent and more amply substantiated value are listed.

b. The heat of this reaction is obtained by combining the heats of reaction 6(a) and 4(a). This reaction does not in any way involve the heat of formation of HF, but in order for it to be valid, the C_2F_4(solid polymer) used in the two different experiments must be similar.

7. Baibuz and Medvedev [14] recalculated the work of Baibuz [13] and reported $\Delta H_f[CF_4(g)] = -220.6$. The work of Baibuz is not available to us in sufficient detail to allow us to write the equation for the reaction or to know the dependence of the reported heat of formation of CF_4 on other auxiliary data.

8. Von Wartenberg [2,4] reported $\Delta H = -307$ kcal mol^{-1}, and although he indicated the carbon was graphite, the evidence from other sources is that probably only a slight amount of graphite was present. On the basis of information supplied by Neugebauer and Margrave (1.5 to 1.9 kcal mol^{-1}) [9], von Wartenberg and Schuette (2.4 kcal mol^{-1}) [1], and Kirkbride and Davidson (2.5 kcal mol^{-1}) [15] if we assume the heat of formation of the carbon residue to be +2 ±1 kcal mol^{-1} and apply a correction, the heat of reaction to that in which graphite is formed would be -307, which is still far less negative than the result of Kirkbride and Davidson.

Kirkbride and Davidson [15] reported $\Delta H_f[CF_4(g)] = -218 \pm 2$ kcal mol^{-1}, together with auxiliary data for XF(c) and amorphous carbon. We have back calculated to obtain $\Delta H_r = -320 \pm 2$ kcal mol^{-1}.

9. Vorob'ev and Skuratov [16] reported $\Delta H_r = -325.5 \pm 2.2$ kcal mol^{-1} and that their reaction led to formation of β-graphite. If we presume, on the basis of the work of Kirkbride and Davidson [15], that only a small amount of crystalline material was present and apply a correction of 2 kcal mol^{-1} for the heat of formation of amorphous carbon, the heat of reaction 9 would be -327.5 kcal mol^{-1}. See 8 above.

References to Table 3

[1] Wartenberg, H. v., and Schutte, R., Z. Anorg. Allgem. Chem. 211, 222-6 (1933).

[2] Wartenberg, H. von, Z. Anorg. Chem. 258, 356-60 (1949).

[3] Ruff, O. and Bretschneider, O., Z. Anorg. Allgem. Chem. 210, 173-83 (1933).

[4] Wartenberg, H. von, Nachr. Akad. Wiss. Goettingen, Math. Physik. Kl, 1946, 57.

[5] Domalski, E. S. and Armstrong, G. T., J. Res. Nat. Bur. Std. 69A, 137-47 (1965).

[6] Domalski, E. S. and Armstrong, G. T., J. Res. Nat. Bur. Std. 71A, 105-118 (1967).

[7] Jessup, R. S., McCoskey, R. E., and Nelson, R. A., J. Am. Chem. Soc. 77, 244-5 (1955).

[8] Duus, H. C., Ind. Eng. Chem. 47, 1445-9 (1955).

[9] Neugebauer, C. A. and Margrave, J. L., J. Phys. Chem. 60, 1318-21 (1956).

[10] Good, W. D., Scott, D. W., and Waddington, G., J. Phys. Chem. 60, 1080-9 (1956).

[11] Scott, D. W., Good, W. D., and Waddington, G., J. Am. Chem. Soc. 77, 245-6 (1955).

[12] Cox, J. D., Gundry, H. A., and Head, A. J., Trans. Faraday Soc. 60, 653-65 (1964).

[13] Baibuz, V. F., Doklady Akad. Nauk S.S.S.R. 140, 1358-60 (1961).

[14] Baibuz, V. F. and Medvedev, V. A., Tr. Gos. Inst. Prikl. Khim., No. 49, 84 (1942).

[15] Kirkbride, F. W., and Davidson, F. G., Nature 174, 79-80 (1954).

[16] Vorob'ev, A. F., and Skuratov, S. M., Zh. Fiz. Khim. 32, 2580-5 (1958).

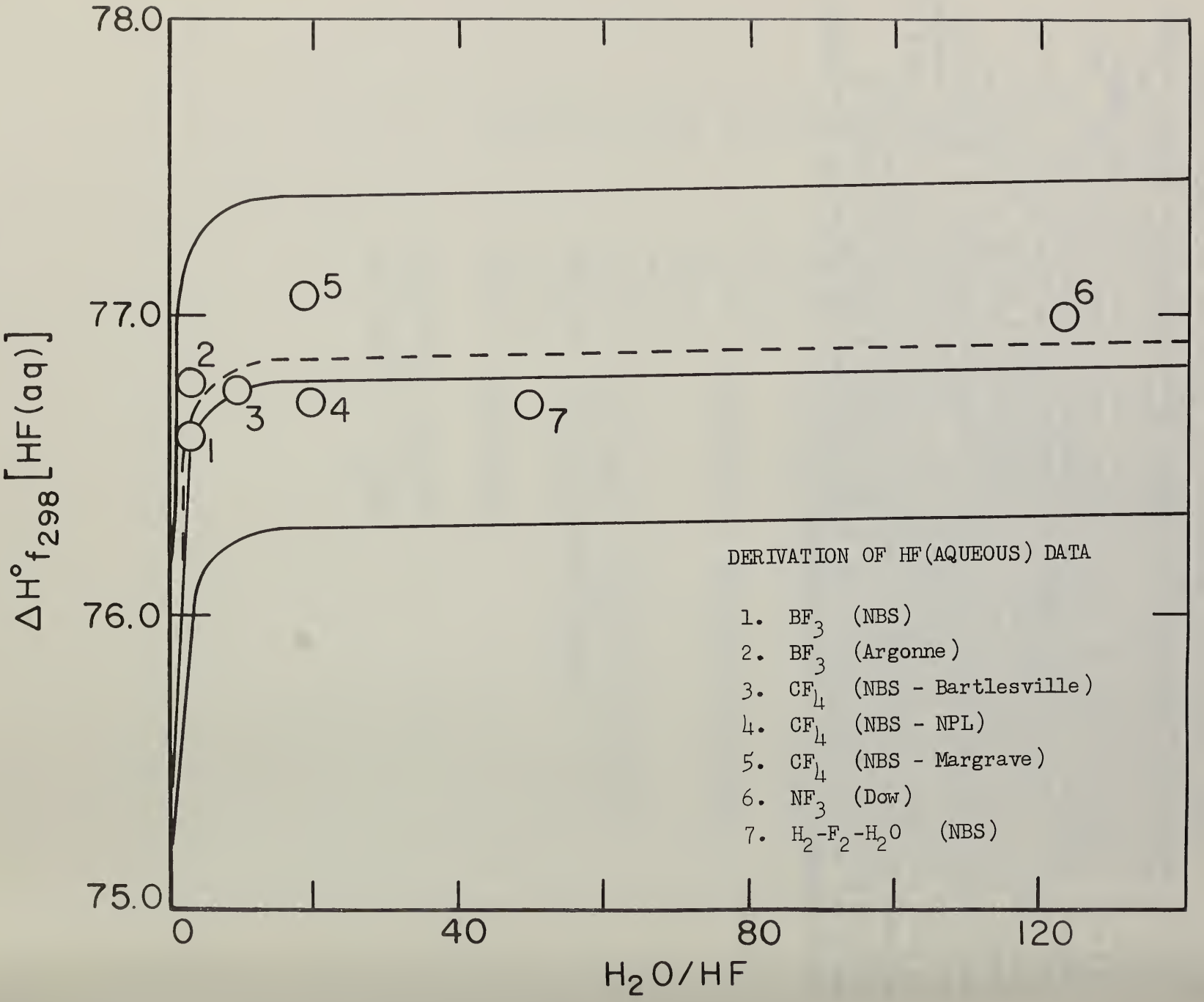
[17] Wood, J. L., Lagow, R. J., and Margrave, J. L., J. Chem. Eng. Data, 1967. In press.

Table 4

Process for $\Delta H_f[CF_4(g)]$ from Reactions of Table 3.

Reaction	
1	$\Delta H_r(1)$
2	$\Delta H_r(2) + \Delta H_f[CH_4(g)] - 4\Delta H_f[HF(g)]$
3(a)	$\Delta H_r(3a) + \Delta H_f[C_2F_4(g)]$
3(b)	$\Delta H_r(3a) - \Delta H_r(3b) + 4\Delta H_f[HF \text{ in } 118.2\ H_2O](\ell)$
3(c)	$\Delta H_r(3a) - \Delta H_r(3c) + 4\Delta H_f[HF](\ell)$
3(d)	$\Delta H_r(3d) + 4\Delta H_f[HF \text{ in } 118.2\ H_2O](\ell)$
3(e)	$\Delta H_r(3e) + 4\Delta H_f[HF(\ell)]$
4(a)	$\Delta H_r(4a) + \Delta H_f[C_2F_4(\text{solid polymer})] - \Delta H_f[CO_2(g)]$
4(b)	See 4(c)
4(c)	$\Delta H_r(4c) + \Delta H_f[CO_2(g)] + 4\Delta H_f[HF \text{ in } 10\ H_2O](\ell)$
5(a)	See 5(c)
5(b)	See 5(c)
5(c)	$\Delta H_r(5c) + \Delta H_f[CO_2(g)] + 4\Delta H_f[HF \text{ in } 20\ H_2O](\ell)$
6(a)	$\frac{1}{2}[\Delta H_r(6a) + \Delta H_f[C_2F_4(\text{solid polymer})]$
6(b)	See 6(c)
6(c)	$\Delta H_r(6c) + \Delta H_f[CO_2(g)]$
7	-
8	$4\Delta H_f[KF(c)] - \Delta H_r(8)$
9	$4\Delta H_f[NaF(c)] - \Delta H_r(9)$

Figure 1. Recent information on the heat of formation of aqueous hydrofluoric acid. Upper curve, Cox and Harrop [19]; Lower curve, Wagman, et al. [21]; A cycle for BF_3-HF set up by Johnson, Feder and Hubbard [15] gives point (1) when applied to data of Domalski and Armstrong [14], and point (2) when applied to data of Johnson, Feder, and Hubbard [15] for BF_3. The heat of formation of CF_4 determined by Domalski and Armstrong [17] by combustion of graphite in fluorine is applied to data relating CF_4 to HF of Good, Scott and Waddington [11] to obtain point (3); to the data of Cox, Gundry, and Head [13] to obtain point (4); and to the data of Neugebauer and Margrave [12] to obtain point (5). A study relating NF_3 to HF reported by Sinke [16] is used to obtain point (6). A study of the H_2-F_2-H_2O reaction by King and Armstrong [18] gives point (7). The central solid curve shows an estimate of the probable best values for $\Delta H_f[HF(aq)]$. The dashed curve differs from the solid central curve by an amount showing the effect of using the heat of formation of CF_4 determined from the combustion of "Teflon" in fluorine [17] on the calculations.


78.0
77.0
76.0
75.0
0
40
80
120
H_2O/HF
$\Delta H^\circ f_{298}$ [HF(aq)]
1
2
3
4
5
6
7
DERIVATION OF HF(AQUEOUS) DATA
1. BF_3 (NBS)
2. BF_3 (Argonne)
3. CF_4 (NBS - Bartlesville)
4. CF_4 (NBS - NPL)
5. CF_4 (NBS - Margrave)
6. NF_3 (Dow)
7. H_2-F_2-H_2O (NBS)

Chapter 2

HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF BERYLLIUM NITRIDE, Be_3N_2, FROM 20 TO 315 K.

George T. Furukawa and Martin L. Reilly

Abstract

The heat capacity of beryllium nitride, Be_3N_2, was determined from 20 to 315 K and the thermodynamic properties calculated from 0 to 315 K. The entropy at 298.15 K was found to be 34.4 ±0.3 J deg^{-1} mol^{-1} (8.23 ±0.08 cal deg^{-1} mol^{-1}).

I. Introduction

The results of heat-capacity measurements on beryllium nitride, Be_3N_2, presented between 20 and 315 K in this paper have been obtained in connection with a research program at the National Bureau of Standards to provide thermodynamic data on light-element compounds. In connection with this program, the high-temperature enthalpy measurements have previously been reported by Douglas and Payne [1]. Earlier, Satoh [9] reported relative enthalpy measurements at three temperatures in the range 273 to 773 K on a sample of 98.13 percent purity, the impurities being 0.78, 0.87, and 0.22 percent BeO, Fe_2O_3, and SiO_2, respectively. Recently Justice [2] reported measurements in the range 25 to 310 K on a sample of 96.7 purity.

II. Apparatus and Method

The low-temperature heat-capacity measurements were made from about 20 to 315 K in an adiabatic calorimeter of a design similar in principle to that described previously [10]. (The measurements were made initially from about 80 K, but the measurements above 315 K were discontinued when small heat effects were observed above 320 K. The results presented in this paper are based on the data obtained subsequent to heating above 320 K.)

The calorimeter vessel, after filling with the Be_3N_2 sample, was sealed by means of a specially designed gold-gasket closure [7] and suspended within the adiabatic shield by means of a Nylon string instead of the filling tube shown in the above reference. The average temperature of the adiabatic shield was sensed relative to that of the

outer surface of the double-walled sample vessel by means of four-junction constantan-Chromel-P thermocouples and was controlled automatically by means of a combination of electronic and electromechanical equipment. Heater wires were wound bifilarly in grooves on the cylindrical surface and on the conical ends of the adiabatic shield to achieve good thermal contact. Details of the design of the calorimeter used, its operation, and the automatic adiabatic control system will be described in a later publication.

The platinum resistance thermometer (laboratory designation: 1057849) used in the measurements was calibrated in accordance with the International Practical Temperature Scale of 1948 [11]. The temperatures in degrees Kelvin (K) were obtained by adding 273.15 deg to the temperatures in degrees Celsius (C). Below 90 K, the thermometer was calibrated on the NBS-1955 provisional scale which is numerically 0.01 deg lower than the former NBS-1939 provisional scale [8]. The NBS-1939 provisional temperature scale is based on a set of platinum-resistance thermometers that were compared against a helium gas thermometer. The thermometer resistance measurements were made to the nearest 0.00001 ohm. Initially a manual Mueller bridge was used and later an automatic Mueller bridge. The resistance-time observations obtained with the automatic bridge were analyzed by means of a computer to calculate the heat capacity. The observations with the manually operated bridge were processed by means of a desk calculator.

The electrical power introduced into the calorimeter heater (100 Ω) was measured by means of a Wenner potentiometer in conjunction with a volt box, standard resistor, and saturated standard cells, which were all calibrated at the National Bureau of Standards. A constant-current power supply stable to 10 ppm or better was used to facilitate the power measurements. The duration of each heating interval was measured by means of a high-precision interval timer operated on the 60-Hz frequency standard provided at the National Bureau of Standards. The 60-Hz frequency standard is based on a 100-kHz quartz oscillator which is stable to 0.5 ppm. An electronic counter containing a 1-MHz interval quartz oscillator was used simultaneously in the measurement of the heating interval. The estimated uncertainty in the determination of the heating interval was not greater than ±0.01 sec for any heating period, none of which was less than 2 min in these experiments.

III. Sample

The Be_3N_2 sample was specially prepared for the measurements by the Brush Beryllium Company, Cleveland, Ohio, by reacting pure nitrogen and beryllium powder at elevated temperatures and crushing the product to particle sizes between 20 and 50 mesh (0.8 and 0.3 mm sieve openings, respectively). The material received was thoroughly mixed in a

controlled-atmosphere box containing dry argon (dew-point: -40 C) and samples were apportioned for chemical analysis, for the high-temperature relative enthalpy measurements [1], and for the low-temperature heat-capacity measurements described in this paper. The samples for the chemical analysis and the high-temperature enthalpy measurements were sealed in test tubes under dry argon. The sample that was poured into the low-temperature calorimeter vessel weighed 97.415g. The calorimeter vessel containing the sample was pumped at high vacuum and purged with dry helium gas several times and finally, helium gas at a pressure of 70 torr was sealed in the container with the sample. After completion of the measurements the calorimeter vessel was opened in the controlled-atmosphere box and the sample was divided and sealed in polyethylene bags for chemical analysis. The sealed polyethylene bags were placed individually in screw-cap jars which were in turn placed in desiccators, the whole operation being done in the controlled-atmosphere box.

The results of spectrochemical analysis of the sample are summarized in Table 1. Only the impurity elements that were detected are listed. The results of the chemical analyses on the material before and after the calorimetric measurements are given in Table 2. For the nitrogen and total beryllium analyses about 0.3 g samples were first dissolved in dilute hydrochloric acid and the solution diluted to 250 cc in a volumetric flask. A 10-cc aliquot was analyzed for nitrogen using the Kjeldahl method, the ammonia being titrated with 0.01 N hydrochloric acid that had been standardized against ammonium dihydrogen phosphate by means of the Kjeldahl procedure. The total beryllium was determined by precipitating the beryllium hydroxide in a 100-cc aliquot with ammonium hydroxide. The beryllium hydroxide was filtered, ignited, and weighed as BeO. The free beryllium was determined by dissolving 2-g samples in hydrochloric acid. The hydrogen formed was dried, converted to water, and weighed.

The analysis for water represents all forms of hydrogen present in the sample. Samples (20 mg) were heated at 1050 C in a carbon-hydrogen-nitrogen analyzer and the amount of water driven off was determined. The oxygen was determined by a non-destructive 14-Mev neutron activation technique. Five determinations were made using 6-g samples.

The results of the chemical analysis were found to be inconsistent and unexpected. The decrease in the free beryllium content in the samples before and after the measurements can not be attributed to chemical reactions at temperatures of the measurements. (Small heat effects were observed above about 320 K. See later parts of this section for further details.) The difference is probably due to non-homogeneity in the material, although relatively large samples (2-g) were used in this determination.

The decrease in the total beryllium content because of a chemical reaction during the heat measurements does not seem possible. If the observed heat effects resulted from a chemical reaction within the sample, the expected reaction would be:

$$3Be(OH)_2 + Be_3N_2 \rightarrow 6BeO + 2NH_3 \ . \qquad (1)$$

This should lead to an increase in the apparent beryllium content, since the ammonia would be lost on opening the sample vessel.

For the material removed from the calorimeter vessel after the heat measurements, the mass balance for beryllium found is not consistent in terms of the analyses obtained. The analyses for N, O, and total Be sum to 100.01 percent and the addition of H (0.13 percent) found as water makes the total weight percent 100.14. This is within the expected limits of accuracy of the chemical analyses. However, inconsistencies arise when these analyses are used to obtain mass balance among the chemical species that are expected to be present (Be_3N_2, BeO, $Be(OH)_2$, and Be metal). On the basis of the results of the oxygen and water analyses (2.38 and 1.14 percent, respectively), the percentage of beryllium as BeO and $Be(OH)_2$ sums to 0.77 percent. When the Be metal (0.04 percent) and beryllium (47.22 percent) as Be_3N_2, based on the nitrogen analysis, are added to 0.77 percent, the total beryllium becomes 48.03 percent. This is considerably lower than the total beryllium (48.70 percent) from the chemical analysis. The masses of the substances present also sum to considerably less than 100 percent (96.15% - Be_3N_2, 2.72% - $Be(OH)_2$, 0.56% - BeO, and 0.04% - Be metal; 99.47% - total mass). These inconsistencies can be resolved if the Be metal analysis were higher (about 0.7 percent), but this is not possible since the estimated error in the chemical analysis for Be metal is much less than this value.

On the other hand, if the analysis shown in Table 2 for water is ignored, the remaining analyses would become consistent on the basis that the substances present are only Be_3N_2, BeO, and Be metal. All of the oxygen (2.38 percent) would then be taken to be present as BeO, which corresponds to 3.73 percent BeO or 1.34 percent Be. When the percentages of Be as Be_3N_2 and as Be metal are added to 1.34 percent, the total "calculated" Be is 48.61 percent. This is within the limits of chemical analysis found for total Be (48.70 percent). When the 96.15 percent Be_3N_2, based on the nitrogen analysis, is added to the percentages of BeO and Be metal, the total weight percent is 99.92 percent. The analyses for total beryllium, nitrogen, and oxygen, as mentioned earlier, sum to 100.01 percent. These values are all within the limits of the chemical analysis.

The source of heat effects observed during the measurements can not be explained in terms of the known possible chemical reaction within the sample. The possible chemical reaction depicted by equation (1), in which the water from $Be(OH)_2$ reacts with Be_3N_2 to form BeO and NH_3, is not consistent with the chemical analyses. The reaction is obviously not possible if the water is securely held at the temperatures of the heat measurements. Duval and Duval [3] interpreted their thermal gravimetric analysis work to indicate that the decomposition of $Be(OH)_2$ starts around 150 C and that complete decomposition of $Be(OH)_2$ to BeO and H_2O occurs only on heating to 951 C. The observed loss in mass at temperatures below 150 C was attributed to adsorbed water in their sample. If any moisture were present in the sample that was used in the work reported here, it was adsorbed between the times the samples was removed from the furnace and received from the supplier.

After careful consideration of the various possibilities that could be selected on the basis of the chemical analyses and the estimated uncertainties that would arise from them, the choice was made to ignore the analysis obtained for water in the reduction of the heat-capacity measurements. The sample was taken to be 96.23 percent Be_3N_2, 3.73 percent BeO, and 0.04 percent Be metal and corrections were applied to the observed values of heat capacity for BeO [5] and Be metal [6].

IV. Results

Two series of measurements were made, one on the calorimeter vessel with sample (gross) and the other on the empty vessel (tare). The measured energy increments (Q) and the corresponding thermometer resistances (R) before and after heating were analyzed on the high-speed digital computer to obtain dQ/dR of the sample as a function of the thermometer resistance [4]. The values of heat capacity (dQ/dT) were then calculated at even temperatures from the dR/dT and the R-T calibration for the thermometer using the relation:

$$dQ/dT = (dQ/dR)(dR/dT) . \qquad (2)$$

Briefly, the procedure was to obtain first the best polynomial equation of the form

$$dQ/dR = \Sigma\, a_n R^n \qquad (3)$$

to represent the experimental data on the empty calorimeter vessel (tare) [12]. The polynomial equation was then evaluated at the thermometer resistances observed for the gross measurements in order to obtain the energy increments for sample only from the observations in the calorimeter vessel plus sample experiments. The best polynomial equation giving dQ/dR for the sample only was then obtained.

Figure 1 shows the deviation of the experimental data on the empty container from corresponding values calculated from the polynomial equation fitted by the method of least squares to the energy-resistance observations. The range of the polynomial is from n = -4 to n = +10 (see eq. 3). Due to increasingly poorer precision at the lowest experimental temperatures the sample data were fitted with two overlapping equations. Figure 2 shows the deviation of the sample data from the polynomial (n ranging from 0 to 4) fitted to the data over the temperature range 20 to 110 K and figure 3 the deviation of the data from the polynomial (n ranging from -2 to +10) fitted over the temperature range 60 to 315 K. Heat capacity values calculated from the two equations agreed within 0.02% over the temperature range 80 to 100 K. The heat capacity values obtained from the two equations were joined at 90 K. Figures 2 and 3 show the precision of the measurements and the effect on the final smooth values of a change of 0.025 percent in the values of the heat-capacity measurements for the empty and filled sample vessel.

As mentioned earlier heat effects were observed during the measurements of the heat capacity above about 320 K, and the results that are presented are based on the data obtained between 20 and 315 K subsequent to heating above 320 K. In figure 4 are shown values of heat capacity initially obtained between 80 and 315 K prior to heating above 320 K. Above 150 K, the values of the initial measurements and those after heating above 320 K are shown to be essentially the same. Below 150 K, the values of the initial measurements are somewhat higher. Since no data were obtained initially below 80 K, no comparison can be made below 80 K between the values before and after heating above 320 K. In the range 80 to 315 K, however, the heating above 320 K did not make a large change in the heat capacity of the sample, at most about 0.5 percent at 110 K. The comparison shows that the heat capacity of the sample was not affected grossly when heated above 320 K.

The values of heat capacity of Be_3N_2, that were generated at evenly spaced temperatures from dQ/dR in accordance with eq (2) were corrected for BeO [5] and Be metal [6] and converted to molal basis. The molecular weight was taken to be 55.05 g. These molal values were analyzed further for extrapolation to 0 K. The final selected values below 20 K are based on the extrapolation of the experimental heat capacity using the Debye heat-capacity function:

$$C = 1943.73\ (705/T)^3 \qquad (4)$$

$$(J\ deg^{-1} mol^{-1})$$

The values of heat capacity from 0 to 315 K were applied in the usual thermodynamic relations:

$$H_T - H^o_{0\,K} = \int_0^T C\, dt \ , \tag{5}$$

$$S_T = \int_0^T (C/T)\, dT \ , \tag{6}$$

and

$$G_T - H^o_{0\,K} = (H_T - H^o_{0\,K}) - T\, S_T \ , \tag{7}$$

to obtain the thermodynamic properties. The values are given in Table 3.

Justice [2] recently reported heat-capacity measurements on α-Be_3N_2 of 96.7 percent purity. The significant impurities were BeO - 2.7%, Be metal - 0.2%, C - 0.1%, and Fe - 0.3%. The entropy at 298.15 K that Justice [2] reported is 8.157 cal deg^{-1} mol^{-1}, which is in good agreement with that (8.23 ±0.08 cal deg^{-1} mol^{-1}) found in this investigation. The values of heat capacity obtained also join satisfactorily, in both the magnitude of heat capacity and its slope, with those derived from the high temperature relative enthalpy measurements reported by Douglas and Payne [1]. A combined table of thermodynamic properties from 0 to 1200 K will be submitted in the next report.

V. References

[1] T. B. Douglas and W. H. Payne, "Be_3N_2 and $BeO{\cdot}Al_2O_3$: High-temperature thermodynamic functions based on recent measurements of heat capacity at the National Bureau of Standards", Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds, NBS Report 7587, 1 July 1962.

[2] Dow Chemical Company, JANAF Thermochemical Tables, Quarterly Supplement No. 25, March 31, 1967, under USAF Contract No. F04611-67-C-0009.

[3] T. Duval and C. Duval, Anal. Chim. Acta, 2, 53 (1948).

[4] G. T. Furukawa and M. L. Reilly, J. Res. NBS 69A (Phys. and Chem.) No. 1, 5 (1965).

[5] G. T. Furukawa and M. L. Reilly, unpublished measurements on BeO.

[6] G. T. Furukawa and M. L. Reilly, unreported results of analysis of literature heat-capacity data on beryllium.

[7] G. T. Furukawa, M. L. Reilly, and J. H. Piccirelli, J. Res. NBS 68A (Phys. and Chem.) No. 4, 381 (1964).

[8] H. J. Hoge and F. G. Brickwedde, J. Res. NBS 22, 351 (1939), RP1188.

[9] S. Satoh, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 34, 888 (1938).

[10] R. B. Scott, C. H. Myers, R. D. Rands, Jr., F. G. Brickwedde, and N. Bekkedahl, J. Res. NBS 35, 39 (1945), RP1661.

[11] H. F. Stimson, J. Res. NBS 65A (Phys. and Chem.) No. 3, 139 (1961).

[12] P. Walsh, Comm. ACM 5, 511 (1962).

Table 1. Summary of Spectrochemical Analysis of the Sample of Beryllium Nitride, Be_3N_2. Impurity Elements that were Detected.

Element	Wt. %	Element	Wt. %
Al	0.001 - 0.01	Mg	0.001 - 0.01
Ca	< 0.001	Mn	< 0.001
Cr	0.001 - 0.01	Ni	0.001 - 0.01
Cu	< 0.001	Si	0.01 - 0.1
Fe	0.01 - 0.1	Ti	0.001 - 0.01

Analysis by: Elizabeth K. Hubbard
Spectrochemical Analysis Section

Table 2. Chemical Analysis of the Sample of Beryllium Nitride, Be_3N_2.

Original Sample

	Wt. %		Wt. %
Be (total)	49.06	N	49.45
	49.09		49.52
			49.84
mean ...	49.08		
		mean ...	49.60
Be (free)	0.09	Cl	<0.02
	0.11		
	0.09	F	<0.01
mean ...	0.10		

Sample Removed from Calorimeter Vessel

Be (total)	48.72	N	48.97
	48.68		48.89
mean ...	48.70	mean ...	48.93
Be (free)	0.04	H_2O	1.16
	0.04		1.12
mean ...	0.04	mean ...	1.14
O	2.38 (average of 5 determinations)		

Chemical analysis by: R. A. Paulson
Microchemical Analysis Section

Oxygen analysis by activation method: S. Nargolwalla
Activation Analysis Section

TABLE 3

THERMODYNAMIC FUNCTIONS FOR BERYLLIUM NITRIDE (BE_3N_2)

SOLID PHASE

GRAM MOLECULAR WT.=55.0500 GRAMS CAL=4.1840 ABS J

T DEG K = 273.15 + T DEG C

T	$-(G_T^0-H_0^C)/T$	$(H_T^0-H_0^C)/T$	$(S_T^0-S_0^C)$	$(H_T^0-H_0^C)$	C_P^0	$-(G_T^0-H_0^C)$
DEG K	CAL / DEG MOLE	CAL / DEG MOLE	CAL / DEG MOLE	CAL / MOLE	CAL / DEG MOLE	CAL / MOLE
.00	.000	.000	.000	.000	.000	.000
5.00	.000	.000	.000	.000	.000	.000
10.00	.000	.000	.000	.003	.001	.001
15.00	.000	.001	.001	.017	.004	.006
20.00	.009	.003	.003	.053	.011	.018
25.00	.002	.005	.007	.129	.021	.043
30.00	.003	.009	.012	.267	.035	.089
35.00	.005	.014	.019	.490	.055	.165
40.00	.007	.021	.028	.828	.081	.280
45.00	.010	.029	.039	1.314	.115	.446
50.00	.014	.040	.053	1.991	.158	.676
55.00	.018	.053	.071	2.910	.212	.985
60.00	.023	.069	.092	4.133	.280	1.390
65.00	.029	.088	.118	5.736	.364	1.913
70.00	.037	.111	.148	7.800	.464	2.575
75.00	.045	.139	.184	10.411	.584	3.404
80.00	.055	.171	.226	13.671	.724	4.427
85.00	.067	.208	.275	17.685	.886	5.677
90.00	.080	.251	.331	22.557	1.066	7.186
95.00	.095	.299	.393	28.379	1.266	8.994
100.00	.111	.352	.464	35.248	1.485	11.134
105.00	.130	.412	.542	43.265	1.725	13.645
110.00	.151	.478	.628	52.531	1.984	16.568
115.00	.173	.549	.722	63.138	2.261	19.941
120.00	.198	.626	.825	75.172	2.555	23.805
125.00	.226	.710	.935	88.715	2.865	28.202
130.00	.255	.799	1.054	103.84	3.188	33.172
135.00	.287	.893	1.181	120.62	3.525	38.755
140.00	.321	.994	1.315	139.12	3.874	44.991
145.00	.358	1.099	1.457	159.38	4.234	51.919
150.00	.397	1.210	1.607	181.47	4.602	59.576
155.00	.439	1.325	1.764	205.42	4.978	68.000
160.00	.483	1.445	1.928	231.26	5.362	77.228
165.00	.529	1.570	2.099	259.04	5.750	87.292
170.00	.578	1.699	2.276	288.77	6.143	98.228
175.00	.629	1.831	2.460	320.47	6.538	110.07
180.00	.682	1.968	2.650	354.15	6.935	122.84
185.00	.738	2.107	2.845	389.83	7.334	136.58
190.00	.796	2.250	3.046	427.49	7.732	151.30
195.00	.857	2.396	3.252	467.14	8.129	167.05
200.00	.919	2.544	3.463	508.78	8.525	183.83
205.00	.984	2.695	3.678	552.39	8.919	201.69
210.00	1.051	2.847	3.898	597.96	9.310	220.63
215.00	1.119	3.002	4.122	645.48	9.698	240.67
220.00	1.190	3.159	4.349	694.93	10.083	261.85
225.00	1.263	3.317	4.580	746.31	10.465	284.17
230.00	1.338	3.476	4.814	799.58	10.843	307.65
235.00	1.414	3.637	5.051	854.73	11.216	332.31
240.00	1.492	3.799	5.291	911.73	11.585	358.17
245.00	1.572	3.962	5.534	970.57	11.950	385.23
250.00	1.654	4.125	5.779	1031.2	12.309	413.51
255.00	1.737	4.289	6.026	1093.7	12.664	443.02
260.00	1.822	4.453	6.275	1157.8	13.012	473.78
265.00	1.909	4.618	6.527	1223.8	13.355	505.78
270.00	1.996	4.783	6.779	1291.4	13.693	539.05
273.15	2.053	4.887	6.939	1334.9	13.902	560.65
275.00	2.086	4.948	7.034	1360.7	14.024	573.58
280.00	2.176	5.113	7.289	1431.6	14.350	609.39
285.00	2.268	5.278	7.546	1504.2	14.670	646.47
290.00	2.362	5.442	7.804	1578.3	14.985	684.85
295.00	2.456	5.607	8.063	1654.0	15.294	724.52
298.15	2.516	5.710	8.226	1702.5	15.486	750.17
300.00	2.552	5.771	8.322	1731.3	15.598	765.48
305.00	2.648	5.934	8.583	1810.0	15.897	807.74
310.00	2.746	6.097	8.844	1890.2	16.187	851.31
315.00	2.845	6.260	9.105	1971.8	16.468	896.18

H_0^C AND S_0^C APPLY TO THE REFERENCE STSTE OF THE SOLID AT ZERO DEK K.

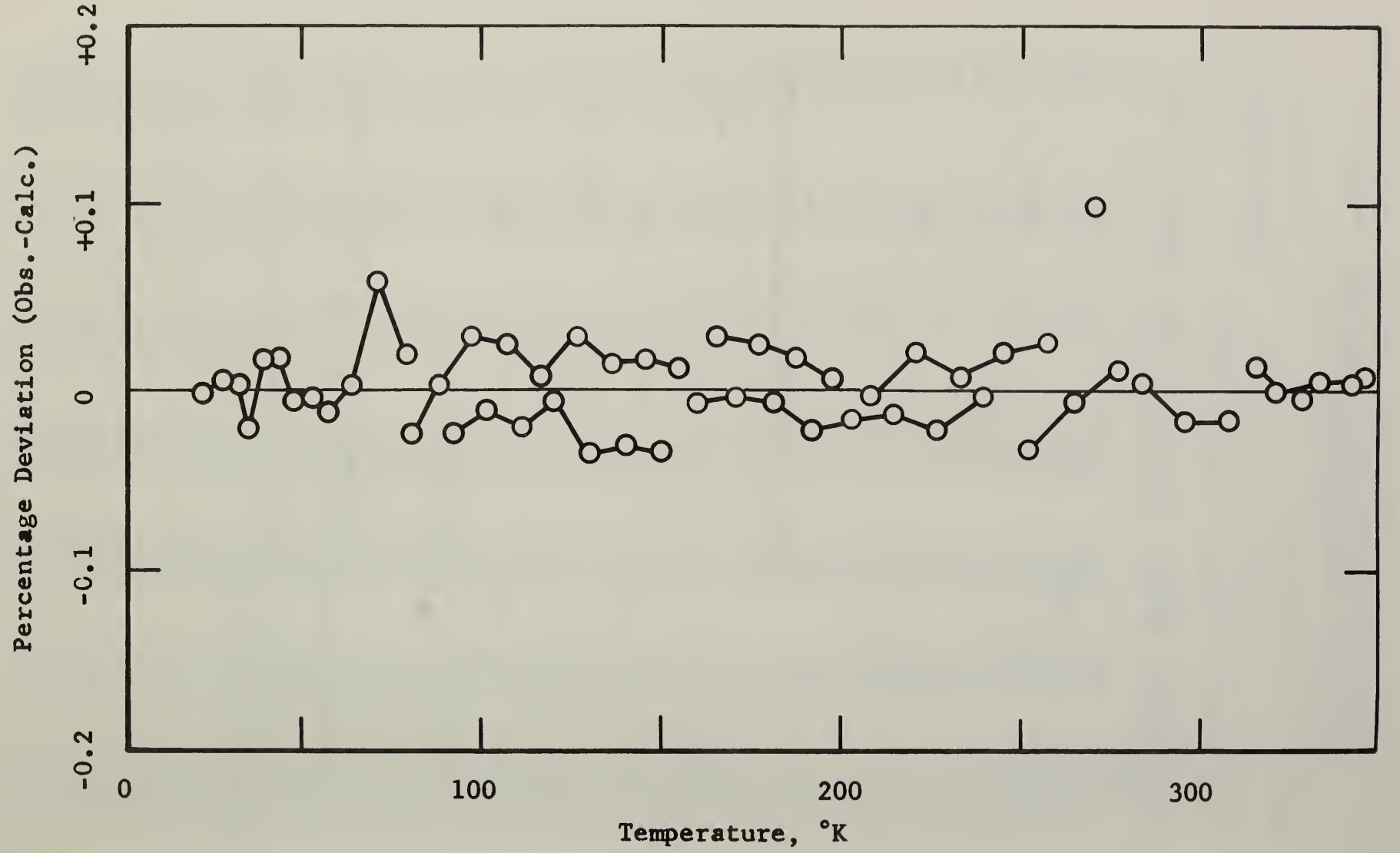


Fig. 1. Percentage Deviation of the Empty Sample Vessel Heat Capacities.

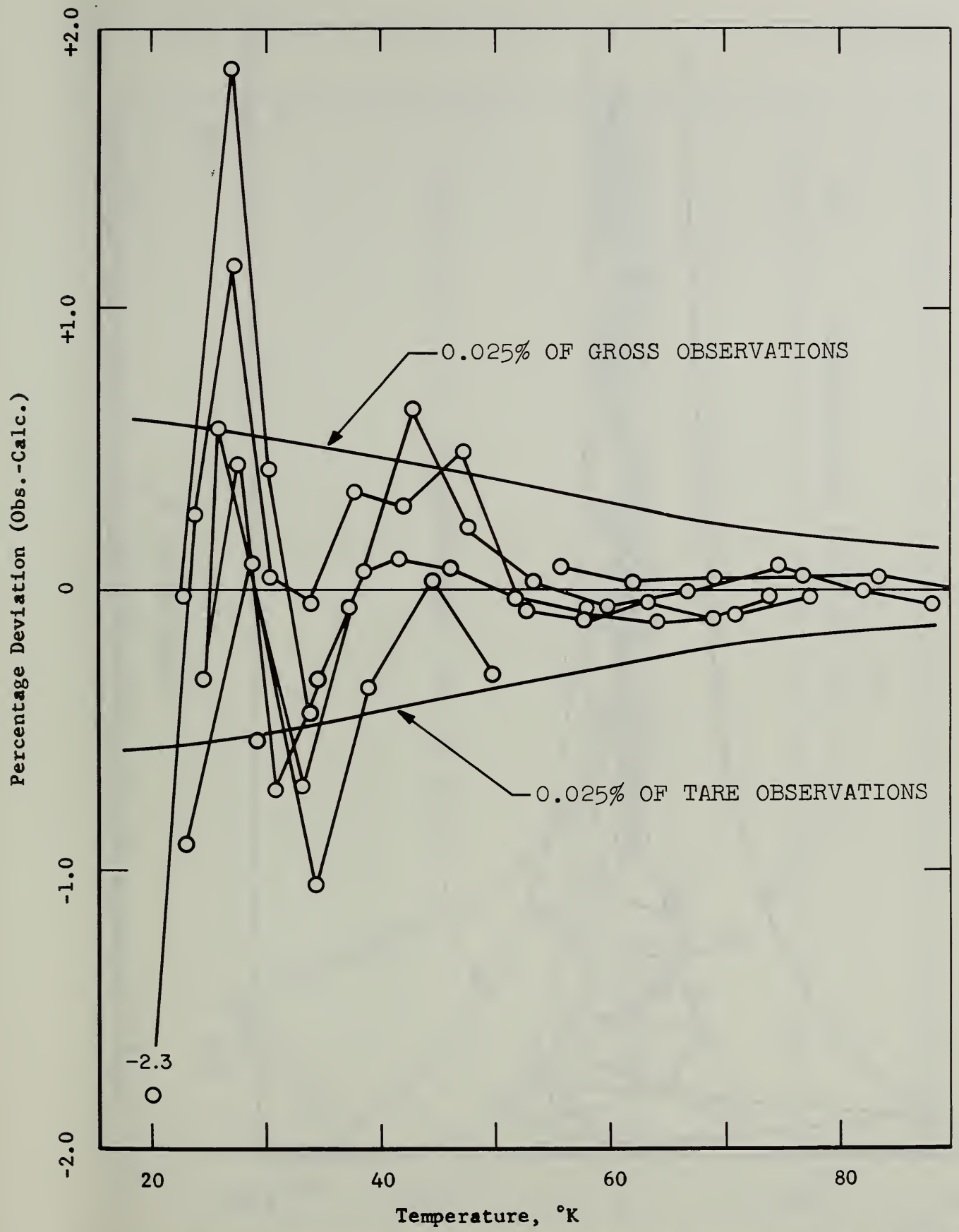


Fig.2. Percentage Deviation of the Beryllium Nitride Sample Heat Capacities.

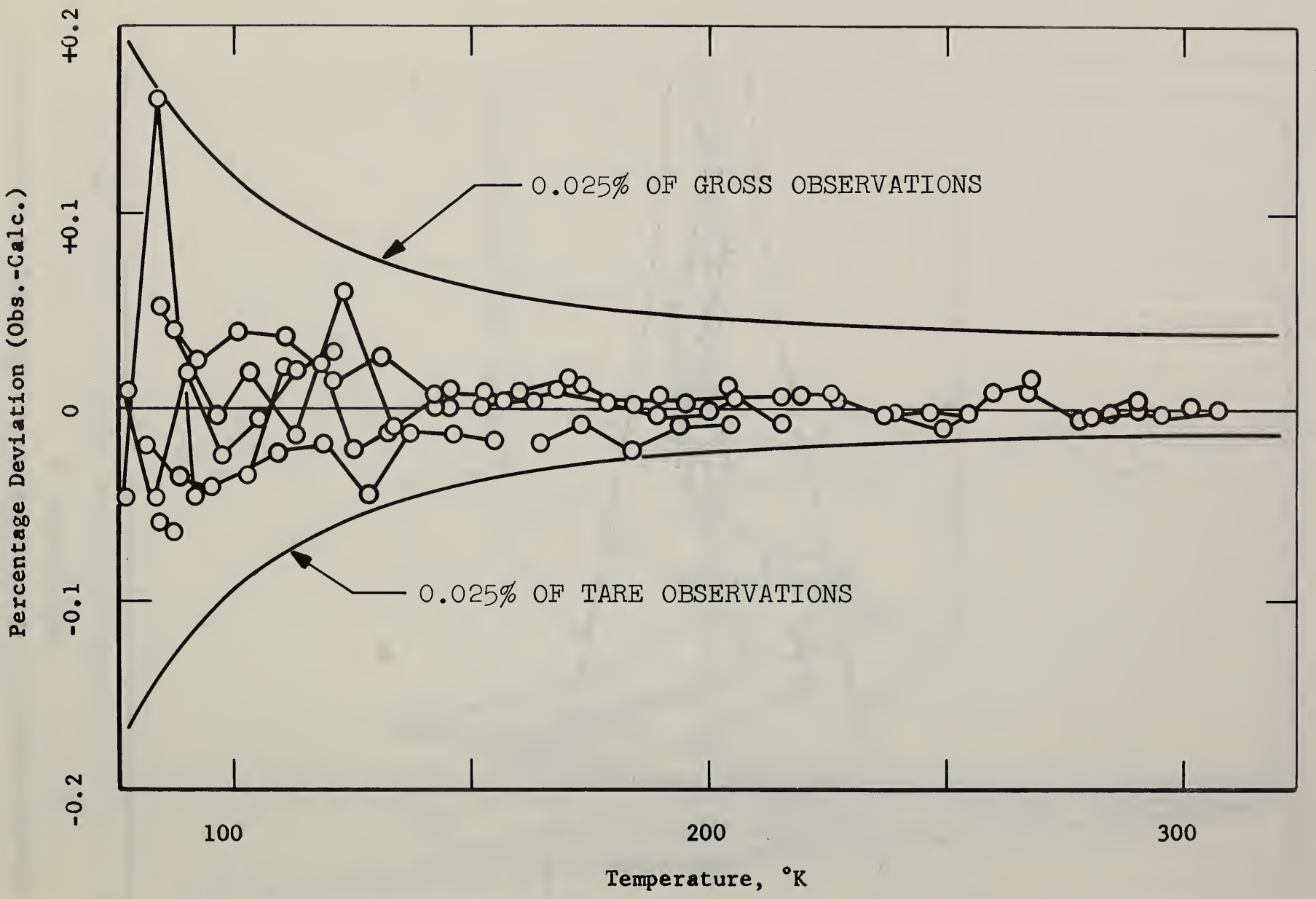


Fig. 3. Percentage Deviation of the Beryllium Nitride Sample Heat Capacities.

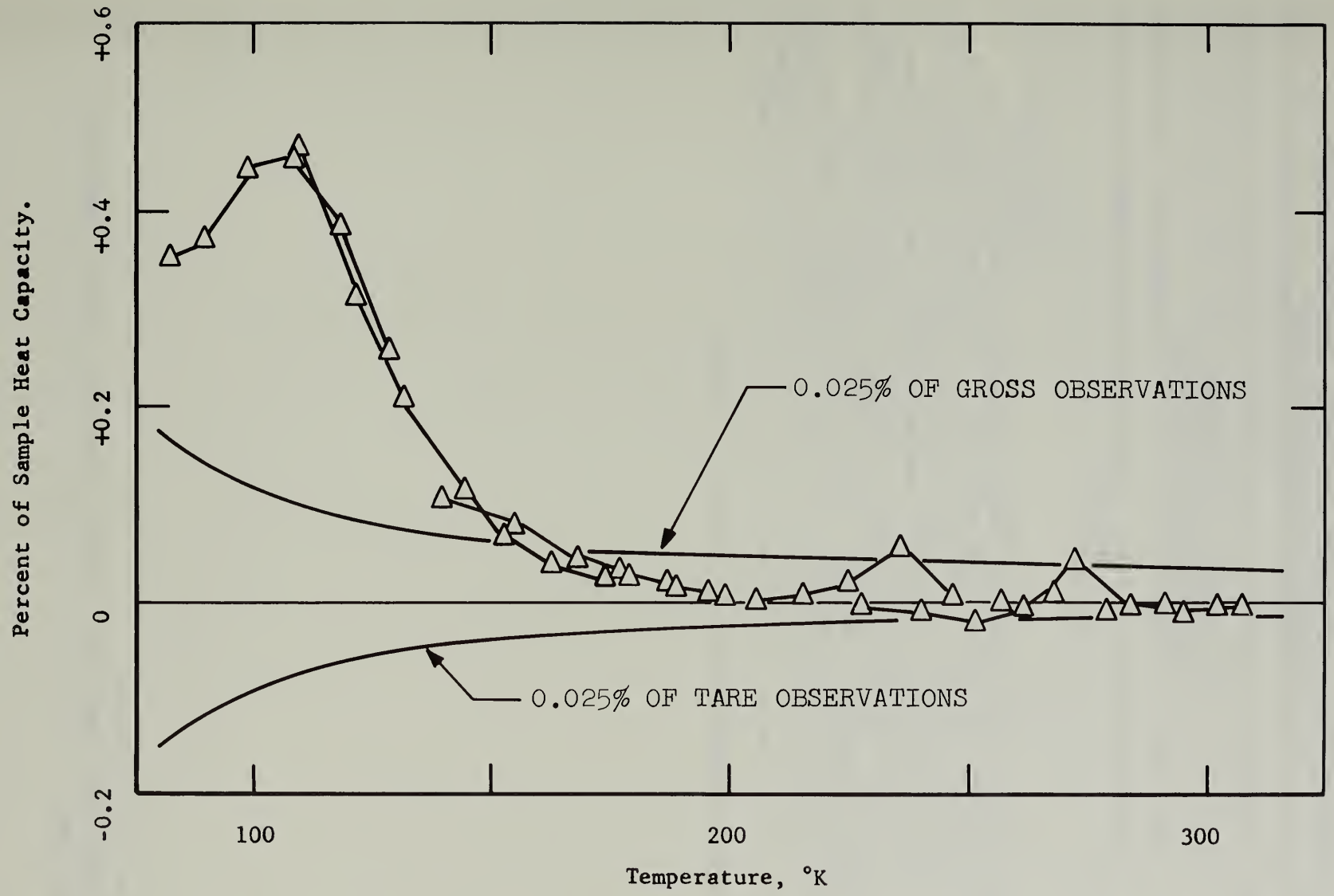


Fig. 4. Percentage Deviation of Initial Measurements from the Beryllium Nitride Sample Heat Capacities.

Chapter 3

AUTOMATIC DATA REDUCTION APPLIED TO BOMB CALORIMETRY OF ORGANIC FLUORINE COMPOUNDS*

George T. Armstrong
Thermochemistry Section

Abstract

Subroutine FARMST, to calculate the combustion energy of organic fluorine compounds from oxygen-bomb calorimetric data, has been prepared following the computational procedure of Good and Scott. The subroutine is written in FORTRAN IV and conforms to the more general program of Shomate for C-H-O-N-S compounds. The Shomate program has been modified to allow introduction of subroutine FARMST, and to change the calculations in several procedural ways including presentation of the result in joules.

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1. Introduction

Shomate [1] prepared a general program for reduction of the data from bomb combustion of organic compounds containing the elements C-H-O-N-S, following the computational procedure of Hubbard, Scott, and Waddington [2]. He recently [1a] modified his program to FORTRAN IV, and segmented it into subroutines. We have made additional modifications in order to improve the versatility of the program, to render the results in joules, and to introduce the new subroutine FARMST.

We have written subroutine FARMST to allow the reduction of data involving fluorine as well as C-H-O-N. For this reduction a procedure for hand computation was previously reported by Good and Scott [3]. This procedure is followed in FARMST. The procedure does not make provision for handling compounds containing both S and F together.

2. New variables in the program

In order to make the general modifications outlined above new variables were defined in the program. Many of these took the form of additions to the array W. It is useful to place variables here because W has the property that it can be modified by the input data cards, and the values in it are available for a memory print-out associated with any experiment. Array W has 999 terms, of which some 673 are used. A complete listing of the variables in this array is given in Table 1. Of these W(1) to W(22), W(109), W(206), W(226), W(246), W(266), W(286), and W(591) to W(673) have not previously been defined. In addition the definitions of W(572) and W(573) were changed. Tables of data needed in subroutine FARMST were introduced into DATA as block data. These are W51AF, a table of solubilities of CO_2 in aqueous HF solutions, obtained from Cox and Head [4]; W87AF, a table of energies of solution of CO_2 in aqueous HF solutions, also obtained from Cox and Head [4]; W71AF, a table of dilution energies for aqueous HF, taken from Wagman, et al. [5]; W72A, W73A, W74A, and W75A, tables of properties of aqueous HF solutions taken from Good and Scott [3]. Unfortunately the latter tables are given only at 25°C, so that the computation is limited in the adequacy with which it can be applied to other temperatures.

Values for the solubility of CO_2 are given by Cox and Head [4] for concentrations of HF from 0 to 5%. Values at 6% were estimated by extrapolation and inserted in the array of data in order to allow use of the quadratic interpolation formulas given in the program for interpolation in the region from 4 to 5 percent. The data for the energy of solution of CO_2 was similarly extrapolated.

Data from Wagman, et al. [5] were smoothed. The point at HF-$10H_2O$ appears to be somewhat irregular and a fictitious value must be used at 0% HF, in order to allow reasonable interpolation from 1 to 2%.

Values at 1 percent intervals were taken from the smooth curve to form the data array to be used in the computations. In all the above cases quadratic interpolation is used. Where temperature is known as a variable, a two-fold quadratic interpolation is used. Table W71AF is not suitable for interpolation in the region 0 to 1% HF.

Table 1.

TABLE OF THERMOCHEMICAL VARIABLES
EXPANDED FOR FARMST SUBROUTINE

Term of the W array	Value or meaning, and units
1	1. The constant unity
2	273.15 The ice point temperature, °K
3	298.15 The standard reference temperature, 25°C.
4	101325 The standard atmosphere, Nm^{-2}
5	22413.6 The standard molar volume of a gas, cm^3
6	4.184 The thermochemical calorie, J
7	
8	The gas constant, R = 8.314325 J mol^{-1}, defined by R = 0.000001 * W(4)/W(2).
9	The gas constant, R = 1.9871715 cal mol^{-1}, defined by R = W(8)/W(6)
10	The gas constant, R = 0.0820560 cm^3 atm, defined by R = W(5)/W(2) * 0.001
11	Molecular weight of water, defined by W(11) = 2. * W(559) + W(560)
12	Molecular weight of carbon dioxide, defined by W(12) = W(558) + 2. * W(560)
13	Molecular weight of nitrous acid, defined by W(13) = W(559) + W(561) + 2. * W(560)
14	Molecular weight of nitric acid, defined by W(14) = W(559) + W(561) + 3. * W(560)
15	Molecular weight of sulfuric acid, defined by W(15) = 2. * W(559) + W(562) + 4. * W(560)
16	Molecular weight of HF, defined by W(16) = W(559) + W(563)
17	
18	
19	
20	

Table 1. (continued).

21	T_h - 25. , defined by W(21) = W(148) - 25.
22	T_h + 273.15, defined by W(22) = W(148) + W(2)
23	Mass of substance
24	Mass of substance
25	Moles of substance
26	V_i[bomb] , dm^3
27	V_i[H_2O(total)] , dm^3
28	P_i[gas] , atm
29	M_i[H_2O(total)] , g
30	N_i[H_2O(total)] , mol
31	V_i[gas] , dm^3
32	N_i[H_2O(vapor)] , mol
33	N_i[H_2O(liquid)] , mol
34	N_i[gas] , mol
35	N_i[(O_2 + N_2) (dissolved)] , mol
36	N_i[O_2 + N_2) (total)] , mol
37	N_f[HNO_3] , mol
38	N_f[HNO_2] , mol
39	N_f[H_2SO_4] , mol
40	N_f[H_2O(liquid)] , mol
41	M_f[solution)]
42	(Weight per cent) $_f$ [H_2SO_4]
43	(Weight per cent) $_f$ [HNO_3 + HNO_2]
44	(Density) $_f$ [solution] , g dm^{-3}
45	V_f [solution]
46	(Normality) $_f$ [H_2SO_4] , mol dm^{-3}
47	(Normality) $_f$ [HNO_3 + HNO_2] , mol dm^{-3}
48	N_f [H_2O (liquid)]/N_f [H_2SO_4]
49	V_f [Gas] , dm^3
50	N_f [CO_2] (total)] , mol
51	K_f [CO_2]
52	D_f [CO_2]
53	K_f^* [CO_2]
54	N_f [CO_2 (dissolved)] , mol
55	N_f [CO_2 (gas)] , mol

Table 1. (continued).

56	N_f [$(O_2 + N_2)$ (total)] , mol
57	K_f [O_2]
58	D_f [O_2]
59	K'_f [O_2]
60	N_f [$(O_2 + N_2)$ (dissolved)] , mol
61	N_f [$(O_2 + N_2)$ (gas)] , mol
62	N_f [gas] , mol
63	X_f [CO_2] , (mole fraction)
64	U_f [gas]
65	P_f [gas] , atm
66	G
67	N_f [H_2O (vapor)] , mol
68	--
69	$[(dE/dp)_T]_f$ [solution] , J mol^{-1} deg^{-1}
70	ΔE (dilution)[$HNO_3 + HNO_2$] , J mol^{-1}
71	ΔE (dilution)[H_2SO_4] , J mol^{-1}
72	--
73	--
74	E [calorimeter] , J deg^{-1}
75	E_i [contents] , J deg^{-1}
76	E_f [contents] , J deg^{-1}
77	ΔE (ignition) , J
78	T_i , deg C
79	T_f , deg C
80	ΔT (correction) , deg
81	$[\Delta E(\text{vaporization})]_i$ [H_2O] , J
82	ΔE_i [H_2O] from 1 to P_i , J
83	ΔE_i [substence] from 1 to P_i , J
84	$[\Delta E \text{ (solution)}]_i$ [$O_2 + N_2$] , J
85	ΔE_i (gas) from 0 to P_i , J
86	ΔE (isothermal bomb process) , J
87	$[\Delta E \text{ (solution)}]_f$ [CO_2] , J
88	$[\Delta E \text{ (solution)}]_f$ [$O_2 + N_2$] , J
89	ΔE_f [solution] from 1 to P_f , J
90	$[\Delta E \text{ (dilution)}]_f$ [$HNO_3 + HNO_2$] , J
91	$[\Delta E \text{ (dilution)}]_f$ [H_2SO_4] , J

Table 1. (continued).

92	$[\Delta E \text{ (decomposition)}]_f [HNO_3 + HNO_2]$, J
93	ΔE_f [gas] from P_f to 0 , J
94	$[\Delta E \text{ (vaporization)}]_f [H_2O]$, J
95	Sum of W (81) to W (94) inclusive, J
96	Combustion energy from auxiliary material , J
97	Combustion energy from fuse , J
98	Combustion energy from compound , J
99	$\Delta Ec/M$ [compound] at T_h , J
100	ΔEc [compound] at T_h , J
101	ΔHc [compound] at T_h , J
102	ΔHc [compound] at 25 deg C , J
103	ΔH_f [compound] at 25 deg C , J
104	A subscript (C_A) in empirical formula of bomb contents
105	B '' (H_B) '' '' '' '' '' ''
106	C '' (O_C) '' '' '' '' '' ''
107	D '' (N_D) '' '' '' '' '' ''
108	E '' (S_E) '' '' '' '' '' ''
109	F '' (F_F) '' '' '' '' '' ''
110	( ) '' ( ) '' '' '' '' '' ''
111	( ) '' ( ) '' '' '' '' '' ''
112	( ) '' ( ) '' '' '' '' '' ''
113	$N_f [N_2^*]$, extra nitrogen , mol
114	Weight of platinum in air , g
115	Weight of glass in air , g
116	Weight of other materials in air , g
117	Mass of platimum (weight in vacuum) , g
118	Mass of glass (weight in vacuum) , g
119	Mass of other materials (weight in vacuum) , g
120	Volume of platinum , dm^3
121	Volume of glass , dm^3
122	Volume of other materials , dm^3
123	Free space in rigid glass bulb , dm^3
124	Nitrogen in free space , mol
125	Initial period rate , deg min^{-1}
126	Final period rate , deg min^{-1}

Table 1. (continued).

127	X [O_2 + N_2] , mole fraction
128	X [N_2^*] , mole fraction
129	Mu [O_2] , see item W(64)
130	A (C_p of solution) , see item W(76) , cal deg^{-1}
131	E [calorimeter] * (T_i - T_f - ΔT (correction)) , J
132	E_i [contents] * (T_i - T_h) , J
133	E_f [contents] * (T_h - T_f + ΔT (correction)) , J
134	ΔH (vaporization) [H_2O] , for W(81) and W(94) ,
135	Cooling constant , min^{-1}
136	Area under Temperature vs. Time curve , deg min
137	Time (start of main period) , min
138	Time (end of main period) , min
139	Temperature (start of main period) , deg
140	Temperature (start of main period) , deg
141	Mid-time (time after start of main period) , min
142	Rotation time , min
143	Heat of bomb rotation , deg min^{-1}
144	Sum of terms W(81) , W(82) , W(84) , W(85) , W(88) , W(89), W(93) , W(94) , W(83) , J
145	Corrected temperature rise , deg
146	Pressure to which the bomb was filled , atm
147	Temperature at which the bomb was filled , deg C
148	T_h , the selected temperature , deg C
149	T_h , predetermined value of T_h , deg C
150	Pressure of N_2 in glass bulb , atm
151	Coefficients used to calculate values of items at temperature T_h from values at 20, 25, and 30 deg C.
152	
153	
154	Selected ratio N_f [H_2O]/N_f [H_2SO_4]
155	Actual ratio N_f [H_2O]/N_f [H_2SO_4]
156	ΔH_f [H_2SO_4] at selected ratio , cal mol^{-1}
157	ΔH_f [H_2SO_4] at actual ratio , cal mol^{-1}
158	Combustion energy from 1st impurity , J
159	Combustion energy from 2nd impurity , J
160	Density of air (if zero , item 567 is used) , g cm^{-3}

Table 1. (continued).

161 C_p of H_2SO_4 solution (selected concentration) , cal g^{-1} deg^{-1}

162 $\Delta C_p/\Delta T$ of H_2SO_4 solution (selected concentration) , cal g^{-1} deg^{-2}

163 Density of H_2O , g dm^{-3}

164 Reference ratio N_f [H_2O]/ N_f [HF]

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Table 1. (continued).

195	
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200	
201	Number of C atoms in compound
202	'' '' A '' '' ''
203	'' '' O '' '' ''
204	'' '' N '' '' ''
205	'' '' S '' '' ''
206	'' '' F '' '' ''
207	'' '' ( ) '' '' ''
208	'' '' ( ) '' '' ''
209	'' '' ( ) '' '' ''
210	Mass of compound (weight in vacuum) , g
211	Molecular weight of compound
212	Moles of compound
213	Density of compound , g cm^{-3}
214	Volume of compound , dm^3
215	Weight of compound (in air) , g
216	C_p of compound , cal g^{-1} deg^{-1}
217	$(\Delta V/\Delta T)_p$ of compound , dm^3 deg^{-1} g^{-1}
218	$(\Delta E/\Delta P)_T$ of compound , J atm^{-1} g^{-1}
219	ΔE_c [compound] , J g^{-1}
220	ΔE_c [compound] , J mol^{-1}
221	Number of C atoms in auxiliary material
222	'' '' H '' '' '' ''
223	'' '' O '' '' '' ''
224	'' '' N '' '' '' ''
225	'' '' S '' '' '' ''
226	'' '' F '' '' '' ''
227	'' '' ( ) '' '' '' ''
228	'' '' ( ) '' '' '' ''
229	'' '' ( ) '' '' '' ''

Table 1. (continued).

230	Mass of auxiliary material (weight in vacuum) , g
231	Molecular weight of auxiliary material
232	Moles of auxiliary material
233	Density of auxiliary material , g cm^{-3}
234	Volume of auxiliary material , cm^3
235	Weight of auxiliary material (in air) , g
236	C_p of auxiliary material, cal g^{-1} deg^{-1}
237	$(\Delta V/\Delta T)_p$ of auxiliary material , dm^3 deg^{-1} g^{-1}
238	$(\Delta E/\Delta P)_T$ of auxiliary material , J atm^{-1} g^{-1}
239	ΔE_c [auxiliary material] , J g^{-1}
240	ΔE_c [auxiliary material] , J mol^{-1}
241	Number of C atoms in fuse
242	" " H " " "
243	" " O " " "
244	" " N " " "
245	" " S " " "
246	" " F " " "
247	" " ( ) " " "
248	" " ( ) " " "
249	" " ( ) " " "
250	Mass of fuse (weight in vacuum) , g
251	Molecular weight of fuse
252	Moles of fuse
253	Density of fuse , g cm^{-3}
254	Volume of fuse , dm^{-3}
255	Weight of fuse (in air) , g
256	C_p of fuse , cal g^{-1} deg^{-1}
257	$(\Delta V/\Delta T)_p$ of fuse, dm^3 deg^{-1} g^{-1}
258	$(\Delta E/\Delta P)_T$ of fuse, dm^3 atm^{-1} g^{-1}
259	ΔE_c [fuse] , J g^{-1}
260	ΔE_c [fuse] , J mol^{-1}
261	Number of C atoms in first impurity
262	" " H " " " "
263	" " O " " " "
264	" " N " " " "

Table 1. (continued).

265	Number of S atoms in first impurity
266	" " F " " " "
267	" " ( ) " " " "
268	" " ( ) " " " "
269	" " ( ) " " " "
270	Mass of first impurity (weight in vacuum) , g
271	Molecular weight of first impurity
272	Moles of first impurity
273	Density of first impurity , g cm^{-3}
274	Volume of first impurity , dm^3
275	Weight of first impurity (in air) , g
276	C_p of first impurity , cal g^{-1} deg^{-1}
277	$(\Delta V/\Delta T)_p$ of first impurity , dm^3 deg^{-1} g^{-1}
278	$(\Delta E/\Delta P)_T$ of first impurity , J atm^{-1} g^{-1}
279	ΔE_c [first impurity] , J g^{-1}
280	ΔE_c [first impurity] , J mol^{-1}
281	Number of C atoms in second impurity
282	" " H " " " "
283	" " O " " " "
284	" " N " " " "
285	" " S " " " "
286	" " F " " " "
287	" " ( ) " " " "
288	" " ( ) " " " "
289	" " ( ) " " " "
290	Mass of second impurity (weight in vacuum) , g
291	Molecular weight of second impurity
292	Moles of second impurity
293	Density of second impurity , g cm^{-3}
294	Volume of second impurity , dm^3
295	Weight of second impurity (in air) , g
296	C_p of second impurity , cal g^{-1} deg^{-1}
297	$(\Delta V/\Delta T)_p$ of second impurity , dm^3 deg^{-1} g^{-1}
298	$(\Delta E/\Delta P)_T$ of second impurity , J atm^{-1} g^{-1}
299	ΔE_c [second impurity] , J g^{-1}

Table 1. (continued).

300	ΔE_c [second impurity] , J mol^{-1}
301 - 400	Recorded times at which corresponding temperature readings in locations 401-500 were taken, minutes
401-500	Recorded temperatures of the initial, main, and final periods, introduced in ohms and converted by the program to degrees C.
501-550	Bridge dial corrections , ohms
551	Ten-ohm dial setting, nominal value, ohms
552	Ten-ohm dial setting correction , ohms
553	Average correction to convert N-only or R-only readings to (N + R) /2.
554	Bridge-zero correction
555	
556	
557	
558	Atomic weight of C (12.01115)
559	Atomic weight of H (1.00797)
560	Atomic weight of O (15.9994)
561	Atomic weight of N (14.0067)
562	Atomic weight of S (32.064)
563	Atomic weight of F (18.9984)
564	Atomic weight of
565	Atomic weight of
566	Atomic weight of
567	Density of Air , 0.0012 g cm^{-3}
568	Density of weights , 8.4 g cm^{-3}
569	Density of platinum ,21.45 g cm^{-3}
570	Density of glass , 2.24 g cm^{-3}
571	Density of other material , 1.0 g cm^{-3}
572	Density of water g/1000 cm^3
573	
574	0.0
575	$\Delta E_c/M$ for benzpic acid calculated by program , J g^{-1}
576	$\Delta E_c/M$ for benzoic acid, certified value = 26.434 kJ g^{-1}
577	C_p of platinum = 0.0325 cal g^{-1}
578	C_p of glass = 0.17 cal g^{-1}

Table 1. (continued).

579 C_p of other material , = 0.0 cal g^{-1}

580 C_p of CO_2, gas, at 25°C , 0.20163 cal g^{-1} deg^{-1}

581 ΔC_p /ΔT of CO_2 = 0.0 cal g^{-1} deg^{-2}

582 C_p of O_2, gas, at 25°C , 0.219375 cal g^{-1} deg^{-1}

583 $\Delta C_p/\Delta T$ of O_2 = 0.0 cal g^{-1} deg^{-2}

584 C_p of N_2, gas, at 25°C, 0.248465 cal g^{-1} deg^{-1}

585 $\Delta C_p/\Delta T$ of N_2 = 0.0 cal g^{-1} deg^{-2}

586 C_p of H_2O, liquid, at 25°C , 0.99895 cal g^{-1} deg^{-1}

587 $\Delta C_p/\Delta T$ of H_2O = 0.0 cal g^{-1} deg^{-2}

588 $\Delta C_p/\Delta T$ of smaple = 0.0 cal g^{-1} deg^{-2}

589 $\Delta H_f[CO_2$ (gas)] = -2137.0552 cal g^{-1}

590 $\Delta H_f[H_2O$ (1)] = -3 792.04 cal g^{-1}

591 ΔH vap [H_2O] = 10 177 cal mol^{-1}

592 ΔE decomp [HNO_3] = 14 074 cal mol^{-1}

593 ΔE decomp [HNO_2] = 6 600 cal mol^{-1}

594 ΔE vap [HF from HF (aq)] = 11 000 cal mol^{-1}

595 ΔE_f [HF in $10H_2O$] = -76 235 cal mol^{-1}

596 ΔH or ΔE hydrolysis [CF_4] = -41 500 cal mol^{-1}

597 C_p [CF_4] = 14.7 cal mol^{-1} deg^{-1}

598 $\Delta C_p/\Delta T$ [CF_4] = 0

599 --

600 --

601 C_i [HF (vap)]

602 $(Normality)_i$ [HNO_3] , m mol cm^{-3}

603 K_i [O_2]

604 N_i [HF (vap)] , mol

605 D_i [O_2]

606 N_f [HF (total)] , mol

607 N_f [CF_4 (total)] , mol

608 N_i [HF (total)] , mol

609 N_f [H_2O (total)] , mol

610 $(Weight\ per\ cent)_f$ [HNO_3]

611 $(Weight\ per\ cent)_f$ [HF]

612 N_f [HF (ag)] , mol

613 N_f [H_2O] /N_f[HF] , actual ratio

Table 1. (continued).

614	N_f [H_2O] / $_f$ [HF] , selected ratio
615	C_f [HF (vap)]
616	$(dE/dp)_i$ [solution] , cal atm^{-1}
617	$(dE/dp)_f$ [solution] , cal atm^{-1}
618	A_i [solution]
619	A_f [solution]
620	N_f [HF (gas)] , mol
621	$(Normality)_f$ [HF] , mmol cm^{-3}
622	ΔE_f [CO_2] /N_f [CO_2] cal
623	Mole fraction (X) [CF_4]
624	ΔE dilution [HF (final)],cal
625	N_f [H_2O] /N_f [HF] , selected ratio
626	Weight per cent HF at selected ratio
627	Weight per cent HF at N_f [H_2O] /N_f [HF] = 10
628	ΔH_f [HF (aq, selected ratio] , cal mol^{-1}
629	N_i [H_2O] , mol
630	ΔH_f [HF (aq, selected ratio)] - ΔH_f [HF (aq, $10H_2O$)] , cal mol^{-1}
631	ΔH_f [HF (aq, $10H_2O$)] - ΔH_f [HF (aq, actual ratio)] , cal mol^{-1}
632	M_i [solution] , g
633	$(\Delta E$ vap$)_i$ [HF] , cal mol^{-1}
634	$(\Delta E$ vap$)_f$ [HF] , cal mol^{-1}
635	ΔE dilution [HF (total)] , cal mol^{-1}
636	M_i [HF] , g
637	Molar coefficient of CF_4 in equation
638	--
639	Correction for CF_4 hydrolysis , cal
640	C_p [HF (aq, selected ratio)] , cal g^{-1}
641	Molar coefficient of O_2 in equation
642	Molar coefficient of H_2O adjusted for hydrolysis of CF_4.
643	Molar coefficient of CO_2 adjusted for hydrolysis of CF_4
644	Molar coefficient of N_2 in equation
645	Molar coefficient of HF adjusted for hydrolysis of CF_4
646	--
647	--

Table 1. (continued).

648	ΔN[gas] , mol
649	ΔH_f [CO_2 (g)] , cal mol^{-1}
650	ΔH_f [H_2O (l)] , cal mol^{-1}
651	Moles idealized actual HF (aq, selected ratio)
652	Moles idealized actual H_2O
653	Moles idealized actual CO_2
654	Moles H_2O reacted (excludes water in HF (aq, selected ratio))
655	M_i [HNO_3] , g
656	$(\text{Weight per cent})_i$ [HF]
657	$(\text{Weight per cent})_i$ [HNO_3]
658	ρ_i [solution] , g cm^{-3}
659	V_i [solution] , 1000 cm^3
660	g_i
661	ΔH at 25° C [adjusted reaction] , J mol^{-1}
662	ΔE at 25° C [adjusted reaction] , J mol^{-1}
663	ΔE at 25° C [unadjusted reaction] , J mol^{-1}
664	ΔH_f [compound] at 25° C, J mol^{-1}
665	ΔE_f [compound] at 25° C, J mol^{-1}
666	ΔH_f [H_2SO_4 (aq, selected ratio)] , J mol^{-1} , = W(156) * W(6)
667	ΔH_f [H_2SO_4 (aq, actual ratio)] , J mol^{-1} , = W(157) * W(6)
668	ΔH [Reaction] at 25° C , adjusted for hydrolysis of CF_4, cal mol^{-1}
669	AE [Reaction] at 25° C , " " " " " cal mol^{-1}
670	ΔE [Reaction] at 25° C , unadjusted , cal mol^{-1}
671	ΔH_f [Compound] at 25° C , cal mol^{-1}
672	ΔE_f [Compound] at 25° C , cal mol^{-1}
673	ΔH [Reaction] at 25° C, unadjusted , cal mol^{-1}

3. Subroutine FARMST

The practice initiated by Shomate, of numbering variables in the W array, so far as possible, to conform to the number of the calculational step given by Hubbard, et al. [2] is continued here by numbering them to conform to the computational steps given by Good and Scott [3]. These authors have made their work mutually consistent to a large degree. It is not possible to follow this practice throughout, however, because in order to retain mutual consistency with Hubbard, et al., Scott and Good introduced multiple variables of the same step number. We have assigned some of these variables higher numbers (above W(590)) more or less as they are encountered in the calculation. The subroutine begins with the calculation of W(29), as all prior steps are identical in the two programs. The subroutine then bypasses the major part of the program called HOWARD, following a parallel but different set of calculations to arrive at final energy values. Where an identity could be established between a variable of FARMST and a variable of HOWARD, i.e. as to meaning, the same variable designation was used in FARMST.

In calculating the composition of the initial bomb contents and the final bomb contents, the program assigns temporary values to the amounts of water and HF present in the liquid phase, and of $CO_2(g)$, $[N_2 + O_2](g)$, $H_2O(g)$, and total gas, present in the gas phase. These are then adjusted after one pass through the calculation, and the calculation of the quantities is repeated.

In mathematical expressions used at various stages of the computations, Good and Scott [3] used expressions valid at 25°C, whereas in similar instances Hubbard, et al. [2] used expressions containing terms with temperature as a parameter. Where the correspondence between equations used showed that the equation used by Hubbard, et al. reduced at 25°C to that used by Good and Scott, we used the more general expression of Hubbard, et al., as did Shomate [1, 1a].

4. Modifications to the main program and subroutines

The modifications made in the main program HOWARD and subroutines INPUT, CONVRT, MIDTIM, OUTPUT, and DATA, may be classified as (1) those necessary to introduce an additional subroutine, which do not modify the mode of calculation, and (2) those which are matters of convenience or preference in causing the calculations to have certain desirable features.

In classification (1) we refer to changes such as program statements necessary to allow the program to recognize the new variables introduced in the subroutine. These are matters of programming technique and include definitions of certain variables at suitable times, in the program or in block DATA subroutine, transfer statements dependent on the presence of F in the compound, and suitable output statements to give the appropriate point out.

In classification (2) changes were introduced in order to change the details of the calculation in certain ways.

Calculations were put in terms of joules wherever practicable. Where input data, such as tables, were in calories in the original sources, these were converted to joules before finally being added as energy terms. The program was restated so that the energy equivalent of the calorimeter would be in joules per degree, the energies of combustion of fuse, auxiliary materials, and impurities were in joules per gram, the ignition energy was in joules, and so on. Output statements were modified to indicate the new units. A certain number of output variables were expressed in both joules and calories, and so new variables were introduced to allow this.

Universal constants and defined constants were introduced in the block data program where possible, rather than as terms in the numerical coefficients of equations throughout the program and subroutines. The algebraic variables were then used in the equations. The reason for this is to permit ready change of a constant throughout the program, if it should ever be desirable. Thus the value of the standard molar volume of a gas, 22413.6 $cm^3\ mol^{-1}$, is given the name W(5), and the

variable W(5) is used wherever the standard molar volume occurs in an equation. A change in the selected value of W(5) is thus readily accomplished. Other universal constants introduced in this way include the ice point, 273.15°K, the standard reference temperature, 298.15°K, the standard atmosphere, 101325 Nm^{-2}, the ratio of the calorie to the joule, 4.184 J cal^{-1}, and the atomic weights of the elements. Derived quantities such as the gas constant, R, and the molecular weights of compounds involved in the calculations are calculated at an early stage of the program HOWARD.

The molar coefficients of the reactions involved and the change in moles of gas present were calculated early in the main program.

In INPUT subroutine a statement is introduced causing the machine to test whether Ti, Tf and ΔT (corr) have been specified. If all three are specified, as by means of a "9" card the program omits their calculation, thus bypassing subroutines CONVRT and MIDTIM.

5. Debugging

Subroutine FARMST and the whole program were "debugged" by running the sample calculation given by Good and Scott [3]. In order to do this, the data used by Good and Scott were carefully examined for conformity to the program requirements. Several adjustments in the program were made temporarily to assure that the program would duplicate the results obtained by Good and Scott. These included setting the density of air equal to zero for the buoyancy correction so that masses instead of weights in air could be used for the amounts of substances introduced. A small discrepancy in the bomb volume (apparently due to neglecting the platinum volume) was discovered. An adjusted bomb volume was then selected. Values of the CO_2 solubility and heat of solution were dubbed in to allow the calculation to simulate Good and Scott's.

6. Input Data Cards

Table 2 gives a printout of the input data cards for a run on perfluoropiperidine. Each card is coded in column 1 with a digit from 1 to 9 which defines the class of information found in it, following Shomate's practice. The "1" card contains data concerning the fuse and auxiliary material. The only deviation from Shomate's practice in the "1" card is the use of energies of combustion of these two substances in joules per gram instead of calories per gram. These values are found in columns 30-35 and 66-72 respectively. The "2" card contains the name of the compound, the numbers of C, H, O, N and S atoms in it, and some bomb conditions. The number of F atoms is introduced later in a "9" card. (Table 2 approximates the card format).

The "3" card contains data on the amounts of substances present. The format of this card has been slightly modified to permit weights to be expressed to micrograms. The revised format is as follows:

Column	Format	Quantity
1		3
2-3	A2	Run Number
4-11	F8.0	Weight of compound (in air), g
12-18	F7.0	Weight of fuse (in air), g
19-25	F7.0	Weight of auxiliary material (in air), g
26-32	F7.0	Weight of platinum (in air), g
33-39	F7.0	Weight of glass (in air), g
40-43	3PF4.0	Volume of water placed in bomb, cm^3
44-48	0PF5.0	Ignition energy, J
49-53	6PF7.0	Moles of HNO_3 formed (X 10^6)
54	F1.0	Moles of HNO_2 formed (X 10^6)
55-59	10PF5.0	Pressure to which bomb is filled, atm

Table 2

```
1  11.774.887     1.5     .4     0.      16945.10   8.      4       1.38       .315.11      22842.2
2  PERFLUOROPIPERIDINE                                5       1  1.730.2514.955  25.
3  1  5.77703     .00114     .12864     19.592     0.0     9.983.72    1149.   40.0025.00
4  28948   1.          1          -            328948  20.
7  THIS IS A SAMPLE OF THE PRINT-OUT OBTAINED FROM THE COMBUSTION PROGRAM.
7  TEST OF FARMST SUBROUTINE USING DATA FROM WD GOOD AND DW SCOTT EXAMPLE
7  TEST OF SHOMATE PROGRAM USING TI, TF, AND DT(CORR) SUPPLIED ON '9' CARD
8  001673
81 001673
9  026  .3538134     074     16746.38     567   0.0
9  078  22.89480     079     24.89078     080   0.00903
9  649-94051.        650-68317.
9  614 10.                                                                606   .045037
9  558  12.010       559  1.008      560  16.000      561 14.008      563  19.00
9  206  11.          226  0.         246  0.          266 0.          286  0.
```

60-64	F5.0	Temperature at which bomb is filled, ^{o}C
65-71	F7.0	Density of air, for reducing weights to vacuum, g cm^{-3}
72	F1.0	Free space, if any, in rigid glass sample bulb, cm^{3}

The moles of HNO_2 formed and the volume of free space in the bulb are usually zero, so those have been reduced to a single column each.

Card "4" contains temperature-time data points. The illustration shows a possible format if Ti, Tf and ΔT (corr) are given. A single temperature and time are given in the initial field (terminated by 1 in column 16) and in the final field (initiated by 3 in column 30). These may not be necessary. The actual values of Ti, Tf and ΔT (corr) are introduced later in a "9" card.

Cards "5" and "6" are not used in this program. Card "7" gives commentary which appears in the printout (see Table 3).

Cards "8" and "81" call for memory printout of the W array, as fixed point and floating point format, respectively. In the example, the W array from W(001) to W(673) inclusive is called for.

Cards "9" are used for direct introduction of values into the W array. The element of the W array is first indicated by its number, then the value to be introduced is listed. In the example, the bomb volume is given in W(026). (This vlaue differs from that used by Good and Scott, by the volume of platinum, which they apparently ignored). The energy equivalent of the calorimeter in joules per degree is given in W(074). A fictitious density of air is given in W(567) to permit masses (weight in vacuum) of the various substances in the bomb to be used as given by Good and Scott.

Ti, Tf, and ΔT (corr) are introduced in W(078), W(079), and W(080), respectively. Enthalpies of formation of carbon dioxide (g), and water (l) are introduced in cal mol^{-1} in W(649) and W(650). W(614) is given the value for the selected ratio of H_2O/HF to be used in the calculations.

Atomic weights used by Good and Scott are introduced in W(558) to W(563). The number of F atoms in the compound of interest is placed in W(206). Other quantities can be introduced at will for checking or other purposes.

7. Output Data

Table 3 is the format of the summary printout of the results of the calculation. Some changes are made from the format suggested by Shomate. The number of decimal figures and the units of several of the quantities are different. Equations are given for the idealized bomb reaction and for the reaction adjusted for hydrolysis of any CF_4 formed. Certain corresponding energy changes are given. In the program these are calculated in joules first and then converted to calories. Values are given at Th and at 298.15°K, which in this case are the same. The results give for the internal energy change of the idealized reaction the value -354.54 kcal mol^{-1}, which may be compared with the value -354.51 given by Good and Scott.

The calculations were compared with those illustrated by Good and Scott at several stages in the development of the program. Only minor differences occur, mostly due to rounding. The difference of the value 354.54 from 354.51 kcal mol^{-1} is apparently due to (1) an error in the value for item 93 listed by Good and Scott, and (2) the use of a different solution energy for CO_2 and a different dilution energy for HF (aq). (Table 3 approximates the actual format).

TABLE 3

PERFLUOROPIPERIDINE

C5 N1 F11 RUN NO. 1

WEIGHT OF SAMPLE (IN AIR) 5.77030 (IN VACUO) 5.777030 GRAMS

INITIAL TEMPERATURE	22.89480	DEG. CENT.
FINAL TEMPERATURE	24.89078	DEG. CENT.
CORRECTION ON TEMPERATURE RISE	.00903	DEG. CENT.
CORRECTED TEMPERATURE RISE	1.98695	DEG. CENT.
COOLING CONSTANT X 10 EXP 3	.000000	PER MIN.
ENERGY EQUIVALENT USED	16746.38	J/DEG

COEFFICIENTS OF IDEALIZED REACTION EXCEPT N2

COMPOUND +	02 +	H2O =	CO2 +	HF . 10H2O +	CF4
1.0000000	2.2500000	23.1701900	2.8016713	2.2066847	2.1983288

STANDARD ENERGY CHANGES OF ABOVE REACTION	JOULES	JOULES/GRAM
INTERNAL ENERGY CHANGE (298.15 DEG K)	-30275.05	-5240.59
	KJ/MOLE	KCAL/MOLE
ENTHALPY CHANGE (298.15 DEG K)	-1475.33	
ENTHALPY CHANGE (298.15 DEG K)	-1475.33	-352.61
INTERNAL ENERGY CHANGE (298.15 DEG K)	-1483.39	-354.54

COEFFICIENTS OF REACTION ADJUSTED FOR HYDROLYSIS OF CF4

COMPOUND +	02 +	H2O =	CO2 +	HF. 10H2O +	N2
1.0000000	2.2500000	115.4999990	5.0000000	10.9999999	.5000000

STANDARD ENERGY CHANGES OF ABOVE REACTION	KJ/MOLE	KCAL/MOLE
ENTHALPY CHANGE (298.15 DEG K)	-1857.04	-443.84
INTERNAL ENERGY CHANGE (298.15 DEG K)	-1865.10	-445.77

Table 3 (continued)

STANDARD ENTHALPY OF FORMATION (298.15 DEG K)	-2047.03	-489.25
STANDARD INTERNAL ENERGY OF FORMATION (298.15)	-2076.78	-496.36
CORRECTION FOR AUXILIARY MATERIAL(S)	-2938.42	JOULES
CORRECTION FOR FUSE	-19.32	JOULES
CORRECTION FOR CARBON DIOXIDE	21.08	JOULES
CORRECTION FOR NITRIC ACID	67.66	JOULES
CORRECTION FOR DILUTION	1.71	JOULES
CORRECTION FOR OTHER REDUCTIONS	74.02	JOULES

CHANGE OF INTERNAL ENERGY FOR ISOTHERMAL BOMB PROCESS IS
-33274.22 -133.88 + 7.12 + 3.72, OR -33397.26 JOULES

MIDTIME .000

THIS IS A SAMPLE OF THE PRINT-OUT OBTAINED FROM THE COMBUSTION PROGRAM

TEST OF FARMST SUBROUTINE USING DATA FROM WD GOOD AND DW SCOTT EXAMPLE

TEST OF SHOMATE PROGRAM USING TI, TF, AND DT (CORR) SUPPLIED ON '9' CARD.

References

[1] C. H. Shomate, "Computer Calculation of Combustion Bomb Calorimetric Data," U. S. Naval Ordnance Test Station Technical Report 327, China Lake, California, August, 1963.

[1a] C. H. Shomate, "Fortran IV Computer Program for Reduction of Heat of Combustion Calorimetric Data," Code 5052 (U. S. Naval Ordnance Test Station, China Lake, California, January 1967).

[2] W. N. Hubbard, D. W. Scott, and Guy Waddington, "Standard States and Corrections for Combustions in a Bomb at Constant Volume," pp. 75-128. "Experimental Thermochemistry," F. D. Rossini, editor, (Interscience Publishers, New York 1956).

[3] W. D. Good and D. W. Scott, "Combustion in a Bomb of Organic Fluorine Compounds," pp. 15-39. "Experimental Thermochemistry, Volume 2," H. A. Skinner, editor (Interscience Publishers, New York 1962).

[4] J. D. Cox and A. J. Head, "Solubility of Carbon Dioxide in Hydrofluoric Acid Solutions," Trans. Faraday Soc. 58, 1839-45 (1962).

[5] D. W. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm. "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-1 (U. S. Government Printing Office, Washington, D. C. 1967). (See also NBS Technical Note 270-3, 1968).

Chapter 4

STRUCTURE OF THE ALKALI HYDROXIDES. III. MICROWAVE SPECTRUM OF GASEOUS RbOH

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The microwave spectrum of gaseous RbOH and RbOD have been studied in a high temperature microwave spectrometer. The spectrum indicates a linear or very near linear molecule with a large amplitude, low-frequency bending vibration. The RbO bond length is 2.30 Å and the OH bond distance is 0.97 Å. The observed frequencies and their assignments for ^{85}RbOH and ^{85}RbOD are given in Table 1. Similar data for ^{87}RbOH and ^{87}RbOD are given in Table 2. The effective rotational constants and nuclear quadrupole coupling constants for various vibrational states of ^{85}RbOH and ^{87}RbOD are found in Table 3. Table 4 gives the values of q for excited vibrational states involving ν_2. A fit of $B_o\nu_2^{\ell}0$ to a power series for ^{85}RbOH and ^{87}RbOD is given in Table 5. Variation of rotational constants with v_1 is shown in Table 6, while the structural parameters found for the species is given in Table 7.

Table I

Observed frequencies in ^{85}RbOH and ^{85}RbOD

$J = 2 \rightarrow 3$

State	$F \rightarrow F'$	^{85}RbOH	^{85}RbOD
$(00^{0}0)$	5/2 5/2	37744.8	
	7/2 (7/2, 9/2)	37741.2	34324.6
	9/2 11/2		
	5/2 7/2	37738.3	34321.6
	3/2 5/2	37734.9	34317.9
	1/2 3/2		
	9/2 (7/2, 9/2)	37728.6	34311.9
$(01^{1}0)$ $\ell+$	5/2 3/2	37600.7	
	3/2 1/2		
	5/2 5/2	37594.3	34301.9
	9/2 11/2		
	7/2 (7/2, 9/2)	37591.3	34299.0
	5/2 7/2	37589.4	34297.3
	3/2 5/2		
	9/2 (7/2, 9/2)	37584.7	34292.3
$(01^{1}0)$ $\ell-$	5/2 3/2	37541.0	
	3/2 1/2		
	5/2 5/2	37534.9	34242.9
	9/2 11/2		
	7/2 (7/2, 9/2)	37532.0	34240.1
	5/2 7/2	37530.6	34238.5
	3/2 5/2		
	9/2 (7/2, 9/2)	37525.5	34233.5
$(02^{0}0)$	7/2 (7/2, 9/2)	37430.5	34242.8
	9/2 11/2		
	5/2 7/2	37417.1	34240.0
	3/2 5/2		(34236.0)
	1/2 3/2		
$(02^{2}0)$	1/2 (1/2, 3/2)	37394.0	34228.8
	3/2 (1/2,3/2,5/2)	37385.2	34220.1
	9/2 (7/2,9/2,11/2)		
	5/2 (3/2,5/2,7/2)	37375.6	34210.4
	7/2 (5/2,7/2,9/2)	37372.2	34207.1
$(03^{1}0)$ $\ell+$	5/2 5/2	37362.2	34278.3
	9/2 11/2		
	7/2 (7/2,9/2)	37358.9	34275.4
	5/2 7/2	37357.2	34273.5
	3/2 5/2		
	9/2 (7/2,9/2)	37352.5	

Table I - cont.

$(03^{1}0)$ $\ell-$	5/2 5/2 9/2 11/2 7/2 (7/2,9/2) 5/2 7/2 3/2 5/2	37238.1 37235.0 37233.0	34152.2 34149.3 34147.8
$(04^{2}0)$	1/2 (1/2,3/2) 3/2 (1/2,3/2,5/2) 9/2 (7/2,9/2,11/2) 5/2 (3/2,5/2,7/2) 7/2 (5/2,7/2,9/2)	37179.4 37170.7 37160.9 37157.8	34189.2 34179.2 34174.8
$(10^{0}0)$	7/2 (7/2,9/2) 9/2 11/2 3/2 5/2 1/2 3/2 9/2 7/2 9/2 9/2	37479.1 37472.7 37466.7	34095.4 34089.0 34082.9
$(11^{1}0)$ $\ell+$	5/2 5/2 9/2 11/2 7/2 (7/2,9/2) 5/2 7/2 3/2 5/2 9/2 (7/2,9/2)	37333.6 37330.8 37329.0 37324.1	34071.0 34068.2 34066.4
$(11^{1}0)$ $\ell-$	5/2 5/2 9/2 11/2 7/2 (7/2,9/2) 5/2 7/2 3/2 5/2 9/2 (7/2,9/2)	37269.2 37266.4 37264.9 37260.0	34010.2 34007.5 34006.1
$(12^{0}0)$	7/2 (7/2,9/2) 9/2 11/2 5/2 7/2	37164.5	34010.5 34007.6
$(12^{2}0)$	1/2 (1/2,3/2) 3/2 (1/2,3/2,5/2) 9/2 (7/2,9/2,11/2) 5/2 (3/2,5/2,7/2) 7/2 (5/2,7/2,9/2)	37140.7 37132.0 37122.3 37119.2	33995.2 33986.8 33977.3 33974.1
(200)	7/2 (7/2,9/2) 9/2 11/2 5/2 7/2 3/2 5/2 1/2 3/2 9/2 (7/2,9/2)	37216.9 37213.9 37210.8 37204.8	33866.8 33863.9 33860.7

Table II

Observed frequencies in ^{87}RbOH and ^{87}RbOD

J = 2 → 3

State	F → F'	^{87}RbOH	^{87}RbOD
(00^00)	7/2 9/2 5/2 7/2	37597.8	34188.4
	3/2 5/2 1/2 3/2	37595.6	34186.6
(01^10) $\ell+$	3/2 3/2	37455.1	
	7/2 9/2 1/2 3/2	37450.8	34165.1
	5/2 7/2 3/2 5/2	37448.7	34163.4
	7/2 7/2	37444.0	
(01^10) $\ell-$	7/2 9/2 1/2 3/2	37391.7	34106.9
	5/2 7/2 3/2 5/2	37389.7	34105.1
(02^00)	7/2 9/2 5/2 7/2	37287.5	34106.9
	3/2 5/2 1/2 3/2	37285.6	34105.2
(02^20)	1/2 3/2	37246.8	
	7/2 (5/2,7/2,9/2)	37241.1	34082.5
	3/2 (3/2,5/2)	37238.3	
	5/2 (3/2,5/2,7/2)	37232.8	34074.2
(10^00)	7/2 9/2 5/2 7/2	37337.1	33960.8
	5/2 7/2 3/2 5/2		33959.0

Table III

Effective rotational constants and nuclear quadrupole coupling constants for various vibrational states of RbOH and RbOD.

State		Bv (^{85}RbOH)	Bv(^{85}RbOD)	eqQ
00^00	Σ	6290.15	5720.77	-67.9
01^10	π	6260.55	5711.69	-67.6
02^00	Σ	6238.37	5707.08	(-67.9)
02^20	Δ	6230.13	5702.57	-67.4
03^10	π	6216.43	5702.34	(-67.6)
04^20	Δ	6194.38	5697.42	-67
10^00	Σ	6246.45	5682.50	-65.9
11^10	π	6216.70	5673.24	-67
12^00	Σ	6194.03	5668.37	(-66)
12^20	Δ	6187.95	5663.75	-66.3
20^00	Σ	6202.75	5644.40	-64.2

State		Bv (^{87}RbOH)	Bv (^{87}RbOD)	eqQ
00^00	Σ	6266.35	5698.13	-35
01^10	π	6236.84	5689.32	-33
02^00	Σ	6214.63	5684.53	-31
02^20	Δ	6206.48	5680.02	-32
10^00	Σ	6222.90	5660.18	(-33)

Table IV

ℓ-Doubling constants

State	q (^{85}RbOH)	q (^{85}RbOD)	q(^{87}RbOH)	q (^{87}RbOD)
$(01^{1}0)$	9.87	9.82	9.85	9.70
$(03^{1}0)$	10.33	10.51		
$(11^{1}0)$	10.73	10.12		

Table V

Fit of $BOv_2{}^2O$ to power series

State	$^{85}RbOH$ calc $BOv_2{}^{\ell}O$	Obs - calc	$^{85}RbOD$ calc $BOv_2{}^{\ell}O$	Obs - calc
00^0O	6290.10	0.05	5720.77	0.00
01^1O	6260.38	0.17	5711.70	-0.01
02^0O	6238.57	-0.20	5707.09	-0.01
02^2O	6230.38	-0.25	5702.49	-0.08
03^1O	6216.48	-0.05	5702.34	0.00
04^2O	6194.10	0.28	5697.45	-0.03

Table VI

Variation of rotational constants with V_1

V_2^{ℓ}	$B0v_2^{\ell}0$	$B1v_2^{\ell}0$
	^{85}RbOH	
0^0	47.70	43.70
1^1	43.85	
2^0	44.34	
2^2	42.18	
	^{85}RbOD	
0^0	38.27	38.10
1^1	38.45	
2^0	38.71	
2^2	38.82	
	^{87}RbOH	
0^0	43.45	
	^{87}RbOD	
0^0	37.95	

Table VII

Structural parameters of Rubidium Hydroxide

	From $B00^{0}0$	From "B_e" [a]
r (RbO)	2.316	2.305
r (ON)	0.913	0.965

a) The first terms in equations (1) were used as "B_e" .

Chapter 5

MASS SPECTROMETRIC STUDY AT HIGH TEMPERATURES OF THE Al_2O_3-BeO SYSTEM

by

J. Efimenko

INTRODUCTION

Data have been obtained for the vapor species existing at high temperatures for a number of selected compositions in the Al_2O_3-BeO system (Report No. 8628, 9028, 9389). This report presents data and calculated thermodynamic quantities for the eutectic mixture, BeO:Al_2O_3 (94.2% Al_2O_3), melting point 1890 ± 10°C, S. M. Lang, C. L. Fillmore, and L. H. Maxwell, J. Res. NBS 48, 301 (1952). The initial purpose of these investigations was to observe and study any complex vapor species in this system. The following is a preliminary report of these data.

EXPERIMENTAL

The procedure followed is similar to that used previously, Report No. 9389. The mass spectrometer had been disassembled completely and reassembled in the new laboratory previous to this experiment. Before the eutectic mixture was placed in the instrument a blank run was carried out. It was necessary to check whether contamination from previously used materials was serious. In addition, a silver calibration was performed in the same effusion cell before the experiment with this eutectic mixture was concluded.

RESULTS

Experimental data are shown in Table 1 and auxiliary data used for computation in Table 2. Equilibria considered for this system are the following:

(1) $Al(g) + O(g) + Be(g) \rightleftarrows AlOBe(g)$
(2) $2Al(g) + O(g) \rightleftarrows Al_2O(g)$
(3) $Al_2O(g) + Be(g) \rightleftarrows AlOBe(g) + Al(g)$
(5) $Al_2O_3.BeO(\ell) \rightleftarrows 2Al(g) + Be(g) + 4O(g)$

Equilibria constants corresponding to these reactions were computed and are presented in Table 3. A second law treatment, (ℓnK vs 1/T)

yielded enthalpies as shown in Table 4. For comparison, enthalpies for the same equilibria, observed over the compound, Al_2O_3.BeO (80.3% Al_2O_3), are presented. On the basis of the reaction enthalpy for (1) this experiment indicates a value of ΔH°_{0f} = -41 kcal/mol for the standard heat of formation of AlOBe. The earlier experiments gave a value of -6.2 kcal/mol.

DISCUSSION

In the temperature range investigated, 2177-2562°K, the only complex specie which appeared in addition to the species from the individual reactants was AlOBe. At the higher end of the temperature range, tungsten oxides appeared also but their intensities were minor in comparison to the species Be^+, O^+, Al^+.

During the period that the data in Table 1 were obtained, two shut-downs occurred. One was to replace the electron bombardment heating filaments that failed and the second was to introduce a weighed quantity of silver for a calibration. The data collected in any one run are indicated by the sequence in the index number and the separate runs by the tens series.

From Table 1 it is observed that there are 34 rows of data to compute enthalpies for reactions 1 and 5, while only eight rows for reactions 2 and 3. Since the specie of interest was AlOBe, more time was spent accumulating data for reactions 1 and 5. One set of data, index numbers 50-57, does not have a temperature cycle.

The computed equilibrium constants for reaction 1 show a rather large scatter for check temperature points. Two factors can be responsible for such a scatter. The effusion cell may have had a serious temperature gradient, before or after changing the bombardment filaments and secondly, temperature equilibrium may not have been established inside the effusion cell. Whenever a temperature cycle was performed during a run, the down temperature data do not always follow the same line as the up temperature data. Attainment of constancy of ion intensity may not be a true indication of thermal equilibrium after intentionally changing temperature. The equilibrium constants for reactions 2 and 3 show much less scatter because no temperature cycle was performed for the data, index numbers 50-57.

Since no composition analysis was made of the condensed phase with time and temperature, reaction 5 will not be discussed here. Using the eutectic composition BeO:Al_2O_3 (94.2% Al_2O_3) gave a starting composition with specific properties at equilibrium. Reaction 3, which is not independent but is obtainable from combination of reactions 1 and 2, is included as a check. These enthalpies need to be re-examined because of the indicated discrepancies. Reaction 2 has been studied independently by other workers, reporting values

ΔH_0°, -254 ± 7 and -243 ± 7 kcal/mol. A third law computation will be made for the enthalpies of these reactions for analysis and comparison. As pointed out previously, the data points for reactions 2 and 3 were taken without a temperature cycle and include much fewer readings. Data were obtained on two other eutectic compositions, BeO:Al_2O_3 (85.9% Al_2O_3) and BeO:Al_2O_3 (75% Al_2O_3), as well as another compound, BeO.Al_2O_3 (80.3% Al_2O_3). This additional data will be analyzed for the same gaseous equilibria.

TABLE 1

Ion Intensities Over Eutectic $BeO:Al_2O_3$ (94.2% Al_2O_3)

(intensities in volts)

Index No.	T, °C	I^+_{Be}	I^+_{O}	I^+_{Al}	I^+_{AlOBe}	I^+_{AlO}	$I^+_{Al_2O}$
57	2190	99×10^{-3}	49×10^{-2}	42×10^{-1}	18×10^{-3}	28×10^{-2}	28×10^{-2}
56	2135	67×10^{-3}	28×10^{-2}	22×10^{-1}	11×10^{-3}	13.5×10^{-2}	14×10^{-2}
55	2085	43×10^{-3}	15.6×10^{-2}	12×10^{-1}	57×10^{-4}	67.5×10^{-3}	73×10^{-3}
54	2030	28×10^{-3}	81×10^{-3}	60.5×10^{-2}	31×10^{-4}	33×10^{-3}	34×10^{-3}
53	1980	16×10^{-3}	38×10^{-3}	27.3×10^{-2}	15×10^{-4}	15×10^{-3}	14×10^{-3}
52	1895	64×10^{-4}	13×10^{-3}	77×10^{-3}	4.5×10^{-4}	14×10^{-4}	32×10^{-4}
51	1855	41×10^{-4}	57×10^{-4}	36.5×10^{-3}	3.5×10^{-4}	9×10^{-4}	12×10^{-4}
50	1850	46.5×10^{-4}	51×10^{-4}	42×10^{-3}	6×10^{-4}	9×10^{-4}	10×10^{-4}
10	1860	33×10^{-4}	8×10^{-3}	39×10^{-3}	72×10^{-4}		
11	1840	27×10^{-4}	51×10^{-4}	21×10^{-3}	45×10^{-4}		
12	1892	51×10^{-4}	81×10^{-4}	61×10^{-3}	57×10^{-4}		
13	1890	45×10^{-4}	93×10^{-4}	63×10^{-3}	45×10^{-4}		
14	2000	14.4×10^{-3}	35×10^{-3}	27×10^{-2}	90×10^{-4}		
15	2050	23×10^{-3}	72×10^{-3}	61×10^{-2}	14×10^{-3}		
16	1985	10×10^{-3}	33×10^{-3}	23×10^{-2}	57×10^{-4}		
17	1930	57×10^{-4}	16×10^{-3}	10×10^{-2}	33×10^{-4}		
18	1880	27×10^{-4}	78×10^{-4}	41×10^{-3}	20×10^{-4}		
20	1860	30×10^{-4}	45×10^{-4}	24×10^{-3}	20×10^{-4}		
21	1920	66×10^{-4}	11×10^{-3}	70×10^{-3}	22×10^{-4}		
22	1880	35×10^{-4}	63×10^{-4}	37×10^{-3}	19×10^{-4}		
23	1850	28×10^{-4}	42×10^{-4}	23×10^{-3}	13×10^{-4}		
30	2055	35×10^{-3}	11.4×10^{-2}	88×10^{-2}	84×10^{-4}		
31	1990	19×10^{-3}	54×10^{-3}	36×10^{-3}	42×10^{-4}		
32	1928	85.5×10^{-4}	19×10^{-3}	12×10^{-2}	20×10^{-4}		
33	1880	54×10^{-4}	10×10^{-3}	54×10^{-3}	14×10^{-4}		

TABLE 1 (continued)

48	1935	59×10^{-4}	24×10^{-3}	11.4×10^{-2}	12×10^{-4}
47	2035	19×10^{-3}	91×10^{-3}	47×10^{-2}	42×10^{-4}
46	2200	10×10^{-2}	67×10^{-2}	55×10^{-1}	28×10^{-3}
45	2150	69×10^{-3}	34×10^{-2}	27×10^{-2}	16×10^{-3}
44	2080	44×10^{-3}	16×10^{-2}	12×10^{-2}	90×10^{-4}
43	2040	26×10^{-3}	80×10^{-3}	61×10^{-2}	52×10^{-4}
42	1975	13×10^{-3}	34×10^{-3}	23×10^{-2}	25×10^{-4}
41	2025	23×10^{-3}	63×10^{-3}	46×10^{-2}	47×10^{-4}
40	1920	72×10^{-4}	17×10^{-3}	89×10^{-2}	11×10^{-4}

TABLE 2

Auxiliary Data

Sensitivity, S_{Ag}	1.7796×10^{-8} amp/mmHg
Temp. - Silver Calib.	1305K
Window + Prism Transmissivity	$1.40 \times 10^{-5} K^{-1}$

Specie	Ionization Cross Section σ_i (1)	Multiplier Sensitivity γ_i (2)
Ag	34.8	296
Be	6.3	276
O	3.3	288
Al	15.4	292
Al_2O	34.1	226
AlOBe	25.0	93

(1) J. W. Otvos and D. P. Stevenson, J. Am. Chem. Soc. 78, 546-551 (1956).

(2) Experimental values, author.

TABLE 3

Equilibria Constants

K_1 subscripts refer to the reactions listed below

Index No.	1/T, °K	K_1	K_2	K_3	$K_5 \times 10^{20}$
57	3.9201	1.2730	3.6402	3.4971	5.7040×10^{-30}
56	4.0128	4.0242	1.2165	3.3082	9.5881×10^{-32}
55	4.1009	1.1166	3.9963	2.7941	1.5154×10^{-33}
54	4.2022	3.7407	1.4808	2.5261	1.5368×10^{-35}
53	4.2985	1.5657	6.6793	2.3441	7.3905×10^{-38}
52	4.4725	1.3175	6.0730	2.1694	2.4400×10^{-41}
51	4.5592	7.9974	2.4020	3.3294	1.1349×10^{-43}
50	4.5703	1.1798	1.6978	6.9490	1.0738×10^{-43}
10	4.5482	1.3564			4.1156×10^{-43}
11	4.5926	3.0777			1.5066×10^{-44}
12	4.4789	4.2548			1.8209×10^{-42}
13	4.4832	3.2166			2.9582×10^{-42}
14	4.2595	1.1251			4.9912×10^{-38}
15	4.1648	2.2541			8.5291×10^{-36}
16	4.2887	1.2952			1.8948×10^{-38}
17	4.3993	6.5663			9.4411×10^{-41}
18	4.5047	4.4072			3.5974×10^{-43}
20	4.5482	1.1973			1.4185×10^{-44}
21	4.4200	7.9299			1.1580×10^{-41}
22	4.5047	4.4311			1.6163×10^{-43}
23	4.5703	9.0211			9.7115×10^{-45}
30	4.1555	3.8737			1.7242×10^{-34}
31	4.2789	1.9521			6.4258×10^{-39}
32	4.4034	1.8653			4.0287×10^{-40}
33	4.5047	9.1351			3.3718×10^{-42}
48	4.3890	1.3427			6.5356×10^{-40}
47	4.1928	8.5192			1.0185×10^{-35}
46	3.9037	1.0857			3.5567×10^{-29}
45	3.9871	3.7652			3.3823×10^{-33}
44	4.1099	1.6873			1.6897×10^{-35}
43	4.1834	6.7253			1.4244×10^{-35}
42	4.3084	4.2802			2.6880×10^{-38}
41	4.2116	1.1728			2.6290×10^{-36}
40	4.4200	1.8497			1.1650×10^{-38}

1. $Al + O + Be = AlOBe$, K_1
2. $2Al + O = Al_2O$, K_2
3. $Al_2O + Be = AlOBe + Al$, K_3
5. $Al_2O_3.BeO(\ell) = Be + 2Al + 4O$, K_5

TABLE 4

Reaction Enthalpies

Results from eutectic $BeO:Al_2O_3$ (94.2 wgt % Al_2O_3, melting point 1890 ± 10°C)

Reaction	ΔH°_{2350}, kcal/mol	ΔH°_0, kcal/mol
(1)	-260	-254
(2)	-262	-256
(3)	+1.82	+1.89
(5)	+980	

Results* from compound $BeO.Al_2O_3$ (80.3 wgt % Al_2O_3, melting point 1870 ± 10°C)

Reaction	ΔH°_{2350}, kcal/mol	ΔH°_0, kcal/mol
(1)	-222 ± 4.6	-216
(2)	-257 ± 6	-252
(3)	+35.5 ± 4	+36.2
(5)	+952 ± 71	

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* From Report No. 9028.

Chapter 6

THE ENTHALPY OF TUNGSTEN FROM 1100 TO 2600°K

E. D. West and S. Ishihara

The high-temperature enthalpy of tungsten is important not only because of its use in high-temperature engineering applications but also because of its use as a container material in the high-temperature enthalpy measurements of other materials and its possible use as a reference material for these measurements to permit a check on the capabilities of various laboratories.

In earlier work in this program [1,2], tungsten was used as a container for liquid Al_2O_3 and liquid $BeO{\cdot}Al_2O_3$. Revised results for the latter are reported in a subsequent chapter in this report.

The work reported in this chapter was carried out as part of a National Bureau of Standards program related to work done for AFOSR.

Method and Apparatus

The method and apparatus have been described briefly [1,2,3]. Essentially, the apparatus consists of a furnace, in which a specimen in a capsule is held at various high temperatures, and an adiabatic calorimeter, operating near room temperature, which measures the heat given up when the hot specimen is lifted into it. Heat lost by the container in the transfer process is accounted for by separate experiments with the empty capsule. If all the heat lost comes from the capsule wall in both experiments, it is accounted for when the difference in heats is ascribed to the specimen.

The temperature in the furnace is measured by a Leeds & Northrup automatic photoelectric pyrometer sighted on the bottom of the capsule. The output signal from the pyrometer is used in a control loop to maintain a selected constant temperature while the capsule is in the furnace. Some improvements have been made in the pyrometry since the earlier report [1]. Frequent balancing of the integrator circuit has apparently improved the precision of the temperature measurement. Reported temperatures are based on a calibration made by the NBS Radiation Thermometry Section in 1967. The conditions of this calibration are closer to the conditions of use than those of the 1965 calibration although the maximum difference between the two is 0.2% at 1108°K. Four spot checks between these two calibrations do not show any consistent trend. They differ from the 1967 calibration by -0.16, -0.95, +0.31 and +0.66°K.

At high temperatures, there is considerable risk of contamination or mechanical damage to both specimen and container. With tungsten we found it helpful to use a smaller specimen for higher temperatures to reduce breakage of the suspension wire. To minimize the risk and permit this flexibility, we use a method which yields in one day's work all the information required for the calculation of the enthalpy at the operating temperature for that day. Usually four experiments are made at the same temperature in a day--two with the capsule alone and two with the capsule plus specimen. For some higher temperatures, only two experiments are made because of the time required for additional weighing. Weights of the capsule and the specimen can be made after each experiment to check for contamination or vaporization. Allowance for variations in the heat for the capsule can be made by correlating weight gains and observed heats for the empty capsule.

A principal advantage of this method is that loss of a capsule or container on one day does not invalidate data taken previously as would be the case if all the data were obtained for the empty capsule before any measurements were made with the specimen. In this case, loss of the capsule might mean loss of the data taken with it. In experiments at 2700°K, a tungsten capsule developed a crack which allowed contamination of specimen D with carbon from the furnace atmosphere, but experiments at lower temperatures were not affected.

Another advantage of the method is that it facilitates intercomparison of different specimens under nearly identical conditions. At 1613°K, for example, two different specimens were used the same day.

Materials

Four specimens were used in this work. These are described below with the same designations used in table 1. All machining was done by grinding with aluminum oxide wheels.

Specimen A: Commercial "pure", nominally 99.95% tungsten. Spectrochemical analysis of another piece of the same rod for 51 elements found a maximum of 0.01% impurity. Surface was cleaned by rinsing in carbon tetrachloride. Weight (corrected for buoyancy) 23.0134 g, constant to 0.2 mg, which is about the limit of the balance used.

Specimen B: Triple zone-refined tungsten nominally 99.999% tungsten, in the form of one-eighth inch diameter rods. The rods were cut to length, but not otherwise machined. The surface was treated with one part 48% HF and two parts concentrated HNO_3 for one minute. The weight was 13.3911 g constant ± within 0.2 mg.

Specimen C: Same as A but surface treated with one part HF and three parts HNO_3. Weight 13.8482 g constant within 0.2 mg until it gained 0.6 mg in the experiment at 2403°K.

Specimen D: Same as C, except weight 10.6807 g. The specimen gained 0.4 mg at 2450°K, 0.4 and 2.9 mg at 2600, 15.5 mg at 2700°K and 20.6 mg at 2800°K. Analysis in a carbon-hydrogen combustion train found 0.74% carbon in a sample 1 mm long cut from the ends of the specimen. A second sample 2 mm long adjacent to the first showed 0.12% carbon. The analysis indicates that carbon vapor reached the specimen through the crack in the capsule wall near one end.

The atomic weight used for tungsten was 183.85.

Results

The corrected experimental data for the enthalpy of tungsten are shown in table 1. Three capsules and four specimens were used, as indicated in the last column. The specimens are described above.

The temperature in the first column has been corrected for the loss of radiation in a prism in the optical path. Corrections made for variation in room temperature in earlier work [1] are no longer necessary.

The quantity of heat in the second column includes corrections for the enthalpy of the capsule and specimen between the actual final calorimeter temperature and 298.15°K. Data required for this correction are taken from Stull and Sinke [4]. Corrections made in the earlier work [1] for small variations in the furnace temperature are no longer required. The enthalpy calculated from one experiment with the capsule and one with the capsule and specimen are shown in the third column.

The data for the enthalpy of tungsten in kilojoules per gram-atomic weight are represented by the equation

$$H_T - H_{298.15} = -7.115 + (23.041)10^{-3}T + (2.9836)10^{-6}T^2 - (.82203)10^{-9}T^3 + (.21967)10^{-12}T^4 \quad \text{kJ/gaw} \qquad (1)$$

The standard deviation is 0.17%. Deviations are shown in the fourth column of table 1.

The table contains data for very pure tungsten (sample B) at four temperatures. The percentage deviations are -0.03, -0.20, +0.09, -0.23, and -0.12. We regard these differences as insignificant and the data for sample B have been used in obtaining equation (1).

One point at 2353°K was omitted in determining equation (1) because it differs by more than three times the standard deviation from the corresponding value from equation (1), although the experiment does not have any apparent defect.

Equation (1) was obtained by the method of least squares, minimizing the sum of the squares of the percentage deviations. This procedure is preferable to working with the deviations themselves because the uncertainty in temperature measurements increases with the temperature. Such a procedure would tend to give too much weight to the experiments at high temperatures.

Discussion

Kirillin, et al. [5] summarize the measurements made before 1963, including their own. They represent the data of several observers with two smoothing equations, one for the range from 250 to 385°K and one from 385 to 3100°K. The maximum difference between their equation and equation (1) is 0.59% at 2050°K. For their data for the range 1275 to 2600°K, the standard deviation is 0.46%. From the deviation plot given [5], it appears that the data in this range are more precise than the standard deviation indicates. For this reason, we have obtained equation (2) for the enthalpy in kilojoules/gram-atomic weight which fits their data for the range 630 to 3093°K with a standard deviation of 0.33%:

$$H_T - H_{298.15} = -3.854 + (25.848)10^{-3}T + (0.72405)10^{-6}T^2 + (.30599)10^{-9}T^3 - .68886\ \ell nT \text{ kJ/gaw} \qquad (2)$$

The difference between equations (1) and (2) is +0.15% at 1100°K, decreasing to -.22% at 1900°K, then increasing to +0.29% at 2500 and 0.51% at 2600°K.

The agreement between the two equations is quite good except at the highest temperature. That agreement is better between equations (1) and (2) than between equation (1) and the equation of Kirillin, et al. [5] indicated that the latter may have given too much weight to older data in the temperature range below 1100°K.

Since tungsten is used as a container for liquid oxides, the data for the enthalpy of tungsten affect the liquid data obtained for $A\ell_2O_3$ and $BeO{\cdot}A\ell_2O_3$ previously reported [1,2]. Revisions of those data are presented in subsequent chapters.

References

[1] E. D. West and S. Ishihara, NBS Report 9028 to AFOSR, 1 January 1966, p. 71.

[2] S. Ishihara and E. D. West, NBS Report 9601 to AFOSR, 1 July 1967, p. 55.

[3] E. D. West and S. Ishihara in "Advances in Thermophysical Properties at High Temperatures and Pressures," Am. Soc. Mech. Engr. 1965, p. 146.

[4] D. R. Stull and G. C. Sinke, Thermodynamic Properties of the Elements, Am. Chem. Soc., Washington, D.C. (1956).

[5] V. A. Kirillin, A. E. Sheindlin, V. Ya. Chekhovskoi, and V. A. Petrov, J. Phys. Chem. USSR 37, 1212, 1963, translated from Zh. Fiz Khim 37, 2249 (1963).

[6] V. Ya. Chekhovskoi, B. Ya. Shumyatskii, and K. A. Yakimovich, Inzh. Fiz. Zh. Akad. Nauk Belorussk SSR 5, 13 (1962).

Table 1. Experimental Data for the Enthalpy of Tungsten [a]

Furn. temp. °K Date of run	Heat to Calorimeter at 298.15°K Joules	$H_T - H_{298.15}$ kJoules/at.wt.	% Deviations Obs-Calc. from eq (1)	Specimen and Capsule Material
1108.8	4599.4	21.299	.02	A, Mo
3-16-66	1933.3			
	1933.3			
	4599.6	21.301	.03	A, Mo
1183.8	2129.6			
2-23-66	5056.6	23.383	-.11	A, Mo
	5055.9	23.413	.02	A, Mo
	2125.2			
1183.8	2121.4			
2-16-66	5050.9	23.403	-.03	A, Mo
	5052.0	23.426	.07	A, Mo
	2119.7			
1333.6	2508.3			
2-14-66	5967.8	27.638	-.09	A, Mo
	5970.0	27.637	-.09	A, Mo
	2510.6			
1405.9	6427.7	29.739	-.03	A, Mo
3-7-66	2705.1			
	2706.7			
	4872.9	29.741	-.03	B, Mo
1514.3	3001.6			
2-11-66	7136.7	33.035	.35	A, Mo
	7142.9	33.027	.33	A, Mo
	3008.8			
1613.2	7758.5	35.747	-.30	A, Mo
3-18-66	3283.9			
	3285.9			
	5892.3	35.784	-.20	B, Mo
1726.8	3605.4			
2-9-66	8529.1	39.335	.12	A, Mo
	8531.2	39.337	.12	A, Mo
	3607.2			
1815.7	9127.9	42.082	.13	A, Mo
3-11-66	3860.3			
	3866.2			
	9109.9	41.891	-.32	A, Mo

Table 1 (Cont'd)

Furn. temp. °K Date of run	Heat to Calorimeter at 298.15 °K Joules	$H_T - H_{298.15}$ kJoules/at.wt.	% Deviations Obs-Calc. from eq (1)	Specimen and Capsule Material
1915.4	4166.9			
3-14-66	9812.0	45.097	-.10	A, Mo
	9827.3	45.245	.23	A, Mo
	4163.8			
1998.1	4400.6			
3-21-66	7883.8	47.821	.09	B, W(1)
	7893.2	47.665	-.23	B, W(1)
	4421.4			
2107.4	8615.3	51.268	-.12	B, W(1)
3-23-66	4753.7			
	4764.4			
	8502.1	51.317	-.03	C, W(1)
2107.5	8874.4	51.155	-.35	C, W(1)
4-18-66	5021.0			
	5023.9			
	8891.8	51.347	-.02	C, W(1)
2210.0	5059.4			
3-31-66	9186.0	54.785	.08	C, W(1)
	9215.1	54.700	-.08	C, W(1)
	5095.0			
2209.1	5078.5			
4-4-66	9215.6	54.924	.38	C, W(1)
(Slow lift	9232.3	54.825	.20	C, W(1)
time)	5102.6			
2267.7	3473.0			
4-14-66	6770.5	56.761	.11	D, W(2)
2300.8	9803.9	57.783	-.09	C, W(1)
4-6-66	5451.5			
2403.3	5944.5			
4-8-66	10569.2	61.394	-.02	C. W(1)

Table 1 (Cont'd)

Furn. temp. °K Date of run	Heat to Calorimeter at 298.15°K Joules	$H_T - H_{298.15}$ kJoules/at.wt.[a]	%Deviations Obs-Calc. from eq (1)	Specimen and Capsule Material
2460.8 4-21-66	4101.4 7799.1	63.649	.30	D, W(2)
2503.1 4-12-66	7741.8 3984.8	64.671	-.48	D, W(2)
2604.4 4-25-66	5167.1 9171.6 8896.6 4912.7	68.931 68.577	.31 -.20	D, W(2) D, W(2)
2353.11* 4-15-66	7126.2 3685.1	59.232	-.70	D, W(2)

[a] Atomic wt. of tungsten 183.85.

* This point was given zero weight for determining the smoothed curve.

Chapter 7

THE ENTHALPY OF SOLID AND LIQUID $BeO \cdot Al_2O_3$ FROM 1200° TO 2400°K - REVISION

S. Ishihara and E. D. West

The data presented[1] for the enthalpy of solid and liquid $BeO \cdot Al_2O_3$

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[1] Ishihara and West, NBS Report 9601 to the AFOSR, 1 July 1967.

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have been revised slightly as a result of a calibration of the automatic pyrometer carried out following completion of the measurements and also as a result of new data for the enthalpy of tungsten, which affects only the data for the liquid. The revisions affect the enthalpy relative to 298.15°K by less than 0.1%. They are therefore probably not important in engineering calculations, but may be useful in checks of consistency of thermodynamic data.

The enthalpy of solid $BeO \cdot Al_2O_3$ from 1180 to 2143°K relative to 298.15°K is given by the equation:

$$H_T - H_{298.15} = -(0.255187)T + (3.46055)10^{-4}T^2 - (1.44123)10^{-7}T^3 + (2.43189)10^{-11}T^4 + 72.2028\ \ell nT - 362.433\ kJ/M \qquad (1)$$

The enthalpy calculated from equation (1) will be approximately 0.05% lower than that calculated from the earlier equation.* With the increased precision from the new calibration, an additional constant is warranted (F test at 95% confidence level).[2] The constants in

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[2] M. G. Natrella, Experimental Statistics NBS Handbook 91 (U.S. Dept. of Commerce, 1963).

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equation (1) are therefore quite different from those in the earlier equation, but the difference in enthalpy calculated is small. Equation (1) fits the data with a standard deviation for an individual measurement of 0.16%, which is very slightly smaller than that given earlier.

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* In the earlier report a minus sign was omitted for the logarithmic term.

The enthalpy of liquid $BeO \cdot Al_2O_3$ has been corrected for new data for tungsten, which was used as a container material, and also for the new pyrometer calibration. The enthalpy for the range 2143 to 2400°K is given by the equation:

$$H_T - H_{298.15} = 1299 - (0.9376)T + (0.2637)10^{-3}T^2 \text{ kJ/M} \qquad (2)$$

The enthalpy calculated from (2) will differ by less than 0.1% from the enthalpy calculated by the earlier equation. The root-mean-square deviation from equation (2) for a single determination consisting of three experiments is 0.03%.

The heat of fusion at 2143°K calculated from the difference between equations (1) and (2) is 172.3 kJ/mole, lower by 1.5 kJ/mole than the value reported earlier. This value depends slightly on the temperature taken for the melting point and increases 0.04 kJ/mole for each degree decrease in the melting point.

Chapter 8

THE STATUS OF THE THERMOCHEMICAL DATA ON SOME Mg COMPOUNDS

by Vivian B. Parker

I Introduction

As part of the revision of NBS Circular 500 "Selected Values of Chemical Thermodynamic Properties", we have completed a review of the available data on all magnesium compounds. We present here a summary of values selected from this review for substances pertinent to the Light Element Thermodynamics Program. We are including also a brief discussion of the sources from which these values have been calculated. It is hoped that this report will indicate where additional research is required. We will appreciate it if data that have been overlooked or errors in the values are brought to our attention before the final tables are published.

All auxiliary data and constants used in the calculations are given in NBS Technical Note 270-3 [1]. All values of $\Delta Hf°$ and $\Delta Gf°$ are in kcal/mol for the molecular formula written and at 298°K, unless otherwise specified. Caution should be exercised if these values must be combined with data taken from other compilations or sources, in order to avoid errors caused by a lack of consistency between the tables.

II Discussion of Data

Mg(c) This is taken as the standard state. The thermal functions were taken from the evaluation of Hultgren et al. [2,3].

Mg(g) The $\Delta H°(subl) = 35.3$ kcal has been taken from the tabulations of Hultgren et al. [2,3], as have the thermal functions of the ideal monatomic gas. Hultgren et al. [3] revised their original selection of 35.3 to 35.0 kcal. We prefer 35.3.

$Mg^{n+}(g)$ The successive ionization energies were taken from Moore [4].

$Mg^{2+}(aq, std. state, m = 1)$ See $MgCl_2(aq)$, $Mg(ClO_4)_2(aq, std. state, m = 1)$ and $Mg(NO_3)_2(aq)$.

Let us first consider $\Delta Hf°$ from the aqueous $MgCl_2$ system. The values given in Table II were corrected to $\Delta Hf°$. Representative values from the $MgCl_2 \cdot 6H_2O$ system are: Samoilov -191.17 kcal; Voskresenskaya and Ponomareva -191.10; Thomsen -191.42; Mishchenko and Yakovlev -191.17. From the $MgCl_2 \cdot 4H_2O(c)$ and $MgCl_2 \cdot 2H_2O(c)$ systems we obtain from Thomsen's measurements -191.77 and -191.20. From $MgCl_2(c)$ we obtain: Mishchenko and Yakovlev -190.92; Mishchenko et al. -191.17; Thomsen -190.28. From Richards et al. we obtain -189.56. A tentative "best" value for $\Delta Hf°$ $MgCl_2$ is -191.22 kcal with $\Delta Hf° Mg^{2+}(aq, std. state, m = 1)$ = -111.32 kcal.

For $Mg(ClO_4)_2$ $\Delta Hf°$ is -173.63 kcal from which we obtain $\Delta Hf° Mg^{2+}$ = -111.81 kcal.

From the $Mg(NO_3)_2$ system, we obtain for $\Delta Hf°$: Pickering -210.67; Thomsen -211.00; Ewing et al. -210.57 and -210.72. These result in a $\Delta Hf°$ = -210.74 and $\Delta Hf° Mg^{2+}$ = -111.62 kcal.

We have selected as "best" value for $\Delta Hf° Mg^{2+}$ -111.58 kcal.

From the solubilities given by Linke [5] and the activity coefficients and osmotic coefficients given by Robinson and Stokes [6] we obtain $\Delta G°soln$ $MgCl_2 \cdot 6H_2O(c)$ = -6.09 kcal and $\Delta G°soln$ $MgSO_4 \cdot 6H_2O(c)$ (metastable at 25°C) = +2.18 kcal. Combined with the appropriate heat of solution data we obtain $\Delta S°soln$ = +6.70 e.u. and -10.64 e.u., respectively. These result in $S° Mg^{2+}$ = -33.1 and -32.5 e.u. We have selected S° = -33.0, with $\Delta Gf° Mg^{2+}$ = -108.7 kcal.

MgO(macrocrystal) and MgO(microcrystal)

The thermal functions for the macrocrystal were taken from the tabulation of the Dow Chemical Co. [7]; those for the microcrystal from the evaluation of Furukawa et al. [8].

There are many determinations for $\Delta Hf° MgO(c)$; however, very few of them distinguish between the macro and micro crystal forms. The following values were reported without any indication which form was

obtained or the percent of each obtained in the direct combustion of Mg(c); Muthman and Weiss [9], -143.0 kcal; Moose and Paar [10] -146.1; von Wartenberg [11] -143.9; Rogers [12] -146.4; Vorob'ev and Skuratov [13] -143.9; Shchukarev et al. [14] -143.23; Holley and Huber [15] -143.65 kcal.

Shomate and Huffman [16] measured the heats of solution of Mg(c) and MgO in aqueous HCl, from which we obtain $Mg(c) + H_2O(liq) \rightarrow MgO(c) + H_2(g)$, $\Delta H° = -75.494$ kcal and $\Delta Hf° = -143.81$. No mention is made of the crystal size of MgO; however, the MgO used was made from igniting $Mg(OH)_2(c)$ at high temperature; the macro crystal form is usually obtained by this method. We are therefore adopting this value as the $\Delta Hf°$ of the macro form. It is the only definite one for all macro MgO(c).

Giauque [17] showed that finely divided MgO prepared from the reduction of $Mg(OH)_2$ at low temperature gives a different S° and ΔH soln in HCl. He reported $\Delta H° = 0.89$ kcal for MgO(macro) → MgO(micro). This results in $\Delta Hf° = -142.92$ kcal.

MgO(g) Brewer and Porter [18] from their vapor pressure measurements have shown that the solid vaporizes mainly into molecular species. They gave spectroscopic evidence that the $^1\Sigma$ electronic state is not the principal vaporizing species. From their measurements and a $^3\Sigma$ ground state we obtain a 3rd law $\Delta H°subl = 129$ kcal, and a $\Delta Hf° = -15$ kcal. From Alexander et al.'s [19] $H_2O(g)$ transpiration study we obtain a 2nd law $\Delta Hf° = -4$ and a 3rd law $\Delta Hf° = +5$ kcal. Altman's [20] Knudsen effusion and O_2 transpiration studies indicate that MgO(g) is of little importance at 2000°K (in contrast to Brewer and Porter) but from the experiments in which $O_2(g)$ is passed over MgO(c) the 3rd law $\Delta H°subl = 162$ kcal and $\Delta Hf° = +18$ kcal. From Porter et al. [21] we obtain $\Delta H°subl > 148.6$ and $\Delta Hf° > 4.8$ kcal.

Bulewicz and Sugden [22] and Veits et al. [23] reported $D°_0 = 98$ and 100 kcal for a $^3\Sigma$ and $^1\Sigma$ ground state, respectively. These result in $\Delta Hf° = -4$ kcal and -2 kcal (corrected to a $^3\Sigma$ ground state).

Drowart et al. [24] used the Knudsen effusion-mass spectrometer technique to determine relative ion intensities and enthalpies for the

reactions $MgO(g) + O(g) \rightarrow Mg(g) + O_2(g)$, and $MgO(g) + WO_2(g) \rightarrow Mg(g) + WO_3(g)$. We obtain, corrected for a $^3\Sigma$ ground state, $\Delta Hf°$ = +12 and +20 kcal from the two reactions.

As is evident, the values are very discordant. We are taking $\Delta Hf°$ = +4 kcal. The uncertainty is large, ±20 kcal.

Brewer and Trajmor [25] feel that for the purposes of high temperature calculations, the most reliable calculations are obtained by the assumption of a $^3\pi$ ground state for MgO(g). This would increase $\Delta Hf°$ approximately 3 kcal.

The thermal functions used in the calculations were obtained from the Dow Chemical Co. [7].

$MgH_2(c)$ The thermal functions were obtained from the Dow Chemical Co. [26] which also cites the references and values obtained for $\Delta Hf°$. We have taken $\Delta Hf°$ = -18.0 kcal.

In addition Pepekin et al. [27] reported $\Delta H°$ = -190.4 kcal for the oxidation of MgH_2 to $MgO(c) + H_2O(liq)$. This results in $\Delta Hf°$ = -21.7 kcal.

$MgOH^+(aq, std. state, m = 1)$ From Sillen and Martell [28] we obtain logK = 2.58 for $Mg^{2+}(aq) + OH^- \rightarrow MgOH^+$. Hostetler's [29] value is in agreement.

$Mg(OH)_2(c)$ The thermal functions were obtained from the Dow Chemical Co. [30].

Wells and Taylor [31] measured the heats of solution of $Mg(OH)_2(c)$ and MgO(macro) in 2N HCl. We obtain for $MgO(c) + H_2O(liq) \rightarrow Mg(OH)_2(c)$, $\Delta H°$ = -9.02 kcal and $\Delta Hf°$ = -221.15 kcal. Similarly, from Taylor and Wells' [32] measurements, we obtain $\Delta H°$ = -9.07, using macro MgO and brucite ($\Delta Hf°$ = -221.20) and -8.83 kcal using macro MgO and synthetic $Mg(OH)_2$ ($\Delta Hf°$ = -220.96 kcal). From Giauque and Archibald [33] we obtain $\Delta H°$ = -9.735 kcal, using micro MgO, and $\Delta Hf°$ = -220.97. Torgeson and Sahama [34] measured ΔH = -26.95 kcal for the solution of synthetic $Mg(OH)_2$ in 1N HCl. Using the results of Shomate and

Huffman [16] on the solution of macro MgO, we obtain ΔH° = -8.84 kcal for the formation of $Mg(OH)_2$ from macro MgO and H_2O(liq) and ΔHf° = -220.97 kcal. From Roth and Chall's [35] measurements we obtain ΔH° = -7.96 kcal and ΔHf° = -220.1 kcal (this is assuming macro MgO(c) is used). We have selected a "best" value of -220.97 kcal.

Giauque and Archibald's decomposition pressure measurements are in agreement with this value. The Dow Chemical Co. [30] cites other decomposition vapor pressure measurements.

$Mg(OH)_2$ppt. From Thomsen's [36] measurements we obtain ΔH = 31.3 kcal for $MgSO_4(400\ H_2O) + 2H_2O$(liq) → $Mg(OH)_2$ppt. + $H_2SO_4(400\ H_2O)$, and 0.7 kcal for $MgSO_4(400\ H_2O) + 2KOH(200\ H_2O) \rightarrow K_2SO_4(800\ H_2O) + Mg(OH)_2$ppt. These reactions result in ΔHf° = -220.5 and -219.8 kcal. From Berthelot's [37] measurements we have ΔH = 0.4 kcal for $MgSO_4(400\ H_2O) + 2NaOH(200\ H_2O) \rightarrow Mg(OH)_2$ppt. + $Na_2SO_4(800\ H_2O)$ and ΔH = 1.5 kcal for $MgCl_2(400\ H_2O) + 2NaOH(200\ H_2O) \rightarrow Mg(OH)_2$ppt. + $2NaCl(400\ H_2O)$. ΔHf°, then, is -220.1 and -219.5 kcal.

$Mg(OH)_2$(aq,std. state, m = 1) The values were obtained from the ions.

$Mg(OH)_2$(g) Alexander et al. [19] determined the Kp's (from 1780°K to 2010°K by the transpiration method) of the reaction $MgO(c) + H_2O(g) \rightarrow Mg(OH)_2(g)$. $\Delta H_{1900^\circ K}$ = 66.8 kcal from which we obtain ΔH° = 67.6 kcal and ΔHf° = -134 kcal.

The values of $H - H_{298}$ used in correcting ΔH to 298°K were taken from the estimated functions of the Dow Chemical Co. [30].

MgF(g) Ehlert et al. [38] reported the K's of the reactions, $AlF_3(g) + 2Mg(g) \rightarrow AlF(g) + 2MgF(g)$ (1238°K to 1301°K), and $2MgF(g) \rightarrow Mg(g) + MgF_2(c)$ (1205°K to 1242°K). Third law values for ΔH° are 47.5 kcal and -126.65 kcal, which lead to -54.1 and -53.3 kcal for ΔHf°. An additional reaction, studied in Ehlert's Dissertation,

is $2MgF(g) \rightarrow Mg(g) + MgF_2(g)$ for which the Dow Chemical Co. [30] reported $\Delta H° = -34.76$ kcal. This results in $\Delta Hf° = -51.5$ kcal.

Gaydon [39] and Herzberg [40] report $D°_0 = 3.2$ ev and 4.2 ev, respectively or $\Delta Hf° = -21$ and -41 kcal.

We have taken $\Delta Hf° = -53.0$ kcal.

The thermal functions were taken from the Dow Chemical Co. [30].

$MgF_2(c)$ The thermal functions were taken from the Dow Chemical Co. [41].

Rudzitis et al. [42], from fluorine bomb calorimetry, reported $\Delta Hf° = -268.7$ kcal. Gross et al. [43] reported $\Delta H° = -109.5$ kcal for $Mg(c) + PbF_2(c) \rightarrow MgF_2(c) + Pb(c)$ which results in $\Delta Hf° = -268.2$ kcal. From Kapustinskii and Samplavskaya [44] we obtain $\Delta H = -94.8$ kcal for $Mg_2SiO_4(c) + 725.2(HF + 4.442\ H_2O) \rightarrow 2MgF_2(c) + H_2SiF_6 + 4H_2O + 715.2(HF + 4.510\ H_2O)$ and $\Delta Hf° = -266.3$ kcal.

From Guntz' [45,46] reactions we obtain $\Delta H = 2.8$ kcal for $MgSO_4(440\ H_2O) + 2KF(220\ H_2O) \rightarrow MgF_2(c) + K_2SO_4(880\ H_2O)$ and $\Delta H = -30.2$ kcal for $MgO + 2HF(110\ H_2O) \rightarrow MgF_2(c) + H_2O$. These result in $\Delta Hf° = -266.7$ and -257.5 kcal, respectively. von Wartenberg [47] reported $\Delta H = -109.6$ kcal for the solution of Mg in aqueous HF, from which we calculate $\Delta Hf° = -262.0$ kcal. Petersen's [48] ΔH for $MgCl_2(440\ H_2O) + 2AgF(220\ H_2O) \rightarrow 2AgCl(c) + MgF_2(c)$ results in $\Delta H = -28.1$ kcal and $\Delta Hf° = -265.2$ kcal. Torgeson and Sahama's [34] reaction of $Mg(OH)_2$ (c, 25°C) with $HF(4.44\ H_2O)$ at 73.7°C results in $\Delta H = -30.9$ kcal and $\Delta Hf° = -267.5$ kcal. We have taken $\Delta Hf° = -268.5$ kcal.

$MgF_2(g)$ The thermal functions used were obtained from the Dow Chemical Co. [30].

There have been many measurements of the vapor pressure over the crystal and liquid. Table I summarizes the 2nd and 3rd law $\Delta H°sub1$ obtained. The "best" value is 95.5 kcal and $\Delta Hf° = -173.0$ kcal.

Table I

Investigator	Temperature °K	Method	ΔH°subl 2nd Law	ΔH°subl 3rd Law
Berkowitz and Marquart [49]	1450	Torsion effusion	91.3	94.68
Green et al. [50]	1241-1492	Knudsen effusion	93.8	96.1
Hammer and Pask [51]	1451-1533(c)	" "	98.8	96.1
	1568-1613(liq)	" "	90.4	96.2
	1413-1518	Torsion effusion	92.9	96.2
	1539-1614	" "	96.4	96.2
Greenbaum et al. [52]	1273-1513	" "	84.0	91.5
Margrave [53]	1241-1492	Knudsen effusion	93.8	96.1
Le Boucher [54]	1934-2129	Manometric	99.9	96.0
Hildenbrand et al. [55]	1425-1533(c)	Torsion effusion	104.8	96.0
	1540-1606(liq)	" "	102.8	95.9
Hildenbrand and Theard [56]	1326-1527(c)	" "	91.5	93.3
	1544-1604(liq)	" "	82.4	95.1
Gunther [57]	1284-1530	Knudsen effusion	95.4	95.6

MgCl(g) Herzberg [40] and Gaydon [39] select D°_0 to be 3.2 ev and 2.7 ev, respectively. These result in ΔHf° = -10 and +1 kcal.

The thermal functions were obtained from the Dow Chemical Co. [41].

$MgCl_2$(c) The thermal functions were obtained from the Dow Chemical Co. [58].

Bommer and Hohman [59] measured the ΔH at 293°K for Mg(c) and $MgCl_2$(c) in 0.1N HCl to be -112.5 and -37.85 kcal, respectively. We obtain ΔH = -74.3 kcal for $Mg(c) + 2HCl(0.1N) \rightarrow MgCl_2(c) + H_2(g)$ and ΔHf° = -153.9 kcal. Similarly Shomate and Huffman [16] obtained, in solutions involving $77.2HCl \cdot 4190\ H_2O$, ΔH = -111.285 and -36.560 kcal, respectively, or ΔH = -74.725 kcal for $Mg(c) + 77.2(HCl + 54.275) \rightarrow MgCl_2(c) + 75.2(HCl + 55.718\ H_2O) + H_2(g)$ and ΔH_f° = -153.28 kcal.

Sano [60] measured the equilibrium $MgCl_2(c) + H_2O(g) \rightarrow MgO(c) + 2HCl(g)$ in the range 796°K to 894°K. We obtain 2nd and 3rd law ΔH° = 19.7 and 23.14 kcal/mol $MgCl_2$ and ΔHf° = -149.9 and -153.28 kcal.

Treadwell [61,62] and Sano [63] measured the equilibrium for $MgCl_2(c) + \frac{1}{2}O_2 \rightarrow MgO(c) + Cl_2(g)$ in the temperature ranges 820°K to 976°K and 865°K to 943°K, respectively. The 2nd and 3rd law $\Delta H°$'s are 9.0 and 9.42 kcal, from Treadwell's measurements, and 8.3 and 9.72 kcal from Sano's, which lead to $\Delta Hf°$ = -152.8 and -153.23, and -152.1 and -153.6 kcal, respectively. Similarly from the results of Tsuchiya [64] in the temperature range 823°K to 973°K we obtain $\Delta Hf°$ = -151.6 and -153.6 kcal from the 2nd and 3rd law approaches. In the temperature range 1013°K to 1153°K ($MgCl_2$(liq)) we obtain $\Delta Hf°$ = -161.6 and -157.6 kcal, respectively. Reznikov's [65] measurements at 1023°K to 1223°K lead to 2nd law and 3rd law $\Delta Hf°$'s = -160.3 and -152.1 kcal, respectively.

Egan et al. [66] from EMF measurements on the reaction $Mg(c) + 2AgCl(NaCl) \rightarrow MgCl_2(c) + 2Ag(c)$ combined with other data on the Ag/(AgCl - NaCl) half cell obtain the $\Delta Gf°$ of $MgCl_2(c)$ at 673°, 723° and 773°K. Their values lead to a 3rd law $\Delta Hf°$ = -154.14 kcal. From the cell measurements of Treadwell et al. [67], Markov et al. [68], Lorenz and Velde [69], and Takahashi [70] on the reaction $Mg(c,liq) + Cl_2(g) \rightarrow MgCl_2(liq)$ we obtain 3rd law $\Delta Hf°$'s = -159.9, -154.9, -152.96, and -153.18 kcal, respectively.

$MgCl_2(g)$ The estimated thermal functions used in the calculations were obtained from the Dow Chemical Co. [7].

Schrier and Clark [71] have shown that the gaseous species over $MgCl_2$(liq), in the range 1200°K to 1400°K, is about 30% dimer. They have also measured the total vapor pressure. Correcting for the dimerization we obtain 2nd and 3rd law $\Delta H°sub1$ = 57.6 kcal and 58.0 kcal, respectively. Using their equilibrium constants for the dimerization process we have corrected the measurements of Kushkin et al.[72] (1173°K to 1323°K) to 43.6 and 57.1 kcal, respectively, the measurements of Fischer et al. [73] (1136°K to 1435°K) to 58.0 and 56.9 kcal, Maier [74] (1056°K to 1400°K) to 50.6 and 57.2 kcal.

Berkowitz and Marquart [49], from Knudsen effusion-mass spectroscopy measurements, reported a monomer pressure at 921°K of 3.84×10^{-5} atm.

and ΔHsubl = 54.6 kcal at 800°K. These measurements result in a 3rd law ΔH° = 56.4 kcal and a 2nd law ΔH° = 55.4 kcal.

Hildenbrand et al. [55] reported vapor pressure results from torsion effusion measurements over the temperature range 800°K to 985°K. Monomeric vapor was assumed. Second and third law ΔH°'s of 61.8 kcal and 57.8 kcal are obtained. We have selected ΔH°subl = 57.6 kcal.

$MgCl_2$(aq, std. state, m = 1) The final values were obtained from the ions. See Mg^{2+}(aq, std. state), $MgCl_2$(aq), $Mg(ClO_4)_2$(aq, std. state, m = 1), and $Mg(NO_3)_2$(aq).

$MgCl_2$(aq) Lange and Streek [75], Zdanovskii and Deryabina [76], Thomsen [36], and Fricke [77] measured ΔHdiln of aqueous $MgCl_2$. Mishchenko and Yakovlev [78] measured the ΔHsoln at varying concentrations.

Measurements of the ΔHsoln $MgCl_2 \cdot rH_2O$(c) lead to the following values for ΔHf (aq, nH_2O), where n is the final concentration. Corrections to 25°C have been made. (See Table II.)

$MgCl_2 \cdot H_2O$(c) The Cp° and S° were obtained from Kelley and King [85].

From Shomate and Huffman's [16] measurements on the solution of Mg(c) and $MgCl_2 \cdot H_2O$(c) we obtain ΔH = -84.157 kcal for Mg(c) + H_2O(liq) + 77.2(HCl + 54.275H_2O) → $MgCl_2 \cdot H_2O$(c) + 75.2(HCl + 55.718H_2O) + H_2(g), and ΔHf° = -231.02 kcal.

$MgCl_2 \cdot 2H_2O$(c) The Cp° and S° were obtained from Kelley and King [85].

As for $MgCl_2$(c) and $MgCl_2 \cdot H_2O$(c) we obtain, from the measurements of Shomate and Huffman [16] ΔH = -90.675 kcal for Mg(c) + 97.2(HCl + 54.275) + 2H_2O(liq) → $MgCl_2 \cdot 2H_2O$(c) + 75.2(HCl + 55.718H_2O) + H_2(g) and ΔHf° = -305.86 kcal.

Auzhbikovich [86] reported ΔH° = 16.4 kcal/mol H_2O for the decomposition of the dihydrate to the anhydrous salt, or ΔHf° = -306.3 kcal.

Table II

System	Investigator	ΔHf kcal/mol	nH_2O	t °C of Meas.
$MgCl_2 \cdot 6H_2O$	1. Samoilov [79]	-190.79	1110	25
	2. Voskresenskaya and Ponomareva [80]	-190.52	333	25
	3. Thomsen [36]	-190.88	400	18
	4. Richardson and Wells [81]	-188.30	22	22.8
	5. Berthelot and Ilosvay [82]	-190.49	200	12.7
	6. Mishchenko and Yakovlev [78]	-190.79	1176	2
		-189.95	52	2
		-187.15	11.45	2
$MgCl_2 \cdot 4H_2O(c)$	1. Thomsen [36]	-191.23	400	18
$MgCl_2 \cdot 2H_2O(c)$	1. Thomsen [36]	-190.66	400	18
$MgCl_2(c)$	1. Mishchenko and Yakovlev [78]	-190.92	2270	2
	2. Mishchenko et al. [83]	-190.8	1110	25
	3. Thomsen [36]	-189.85	800	18
Mg(c) + equiv. am't. $HCl \cdot 200\ H_2O$	1. Richards et al. [84]	-189.56	400	20

$MgCl_2 \cdot 4H_2O(c)$ The Cp° and S° were obtained from Kelley and King [85].

As for $MgCl_2 \cdot 2H_2O(c)$, we obtain, from Shomate and Huffman's [16] measurements $\Delta H = -102.056$ kcal for $Mg(c) + 77.2(HCl + 54.275) + 4H_2O(liq) \rightarrow MgCl_2 \cdot 4H_2O(c) + 75.2(HCl + 55.718\ H_2O)$ and $\Delta Hf° = -453.87$ kcal.

Kondirev and Berezovskii [87], Derby and Yngve [88], Sano [89], and Auzhbikovich [86] measured the decomposition pressure of the hexahydrate to the tetrahydrate. A log p vs 1/T plot of the data results in $\Delta Hf° = -453.99$ kcal.

Kondirev and Berezovskii [87] and Sano [90] measured the decomposition pressures of the tetrahydrate to the dihydrate. A log p vs 1/T plot results in $\Delta Hf°$ = -454.05. Auzhbikovich's measurements result in $\Delta Hf°$ = -457.1.

$MgCl_2 \cdot 6H_2O(c)$ The Cp° and S° were obtained from Kelley and King [85].

As for $MgCl_2 \cdot 4H_2O(c)$ we obtain from Shomate and Huffman's [16] measurements ΔH = -108.836 kcal for Mg(c) + 77.2(HCl + 54.275) + $6H_2O$ (liq) → $MgCl_2 \cdot 6H_2O(c)$ + 75.2(HCl + 55.718 H_2O) and $\Delta Hf°$ = -597.28 kcal.

$Mg(ClO_4)_2(c)$ Vorob'ev et al. [91] reported ΔHsoln in 800 H_2O to be -37.08 kcal. This results in $\Delta Hf°$ = -135.97 kcal. Drakin and Chzhan [92] reported four measurements in the range from m = .02 to .09 (where m is the molality), which lead to $\Delta Hf°$ = -135.68 kcal. Smeets' [93] measurements for m = 0.12 result in $\Delta Hf°$ = -135.53 kcal. Measurements have also been reported by Smith et al. [94]. We have selected the first mentioned value.

$Mg(ClO_4)_2$(aq, std. state, m = 1) The final values were obtained from the ions. See Mg^{2+}(aq, std. state, m = 1), $MgCl_2$(aq) and $Mg(NO_3)_2$(aq).

Jongenburger and Wood [95] measured the ΔH diln from 3.2 to .0018 molal.

Vorob'ev et al. [91] reported ΔH = -36.11 kcal for the reaction, $MgO(c) + 2HClO_4 \cdot 800\ H_2O \rightarrow Mg(ClO_4)_2 \cdot 800\ H_2O + H_2O$. This results in ΔHf = -173.28 kcal for $Mg(ClO_4)_2 \cdot 800\ H_2O$ and $\Delta Hf°$ = -173.63 kcal.

$Mg(ClO_4)_2 \cdot 6H_2O(c)$ Smeets [93] reported measurements of ΔHsoln at 18°C for the hexahydrate and the anhydrous salt. We obtain $\Delta H°$ = -38.71 kcal for $Mg(ClO_4)_2(c) + 6H_2O(liq) \rightarrow Mg(ClO_4)_2 \cdot 6H_2O(c)$ and $\Delta Hf°$ = -584.57 kcal. Similarly from Smith et al. [94] we obtain $\Delta H°$ = -32.7 kcal and $\Delta Hf°$ = -578.6 kcal. Their value for ΔH soln = 0.8 kcal for the hexahydrate leads to $\Delta Hf°$ = -583.8 kcal. Nosova [96] reported ΔH soln to a final concentration of 0.07 m = 1.45 kcal, from which we obtain $\Delta Hf°$ = -584.39 kcal.

Linke [5] lists the saturation concentration to be 4.48 molal. Using this and the activity coefficient and osmotic coefficient from Robinson and Stokes [6] we obtain $\Delta G°soln$ = -7.60 kcal, which results in $\Delta Gf°$ = -445.34 kcal and S° = 124.5 e.u.

MgOHCl(c) Kelley [97] evaluated the data on the MgOHCl(c) system and obtained for $MgCl_2 \cdot H_2O(c) \rightarrow MgOHCl(c) + HCl(g)$ $\Delta H°$ = 17.82 and $\Delta G°$ = 8.34 kcal. These lead to $\Delta Hf°$ = -191.1 kcal, $\Delta Gf°$ = -174.9, and S° = 20.0 e.u.

Savinkova and Dagtyareva [98] reported the equilibrium from 743°K to 1023°K for $MgCl_2$(solid soln) + $H_2O(g) \rightarrow$ MgOHCl(solid soln) + HCl(g). The K's include the activities. Their results give $\Delta H°$ = -1.5 kcal and $\Delta Hf°$ = -191.1 kcal. Vel'nyanskii and Savinkova [99] do not give the activities; hence, their values have not been used.

$MgBr_2$(c) Beketov [100] reported ΔHsoln in 800 H_2O = -43.30 kcal, from which we obtain $\Delta Hf°$ = -125.26 kcal. Finch et al. [101] report ΔH = -35.23 kcal for the reaction of MgO(c) in excess HBr(m = 0.5) to form $MgBr_2 \cdot 2000\ H_2O$, and ΔH = -43.14 kcal for the solution of $MgBr_2$(c) in excess HBr(m = 0.5) to form $MgBr_2 \cdot 9000\ H_2O$. Correcting for the concentration change, we obtain ΔH = 7.78 kcal for $MgO(c) + 2HBr(aq) \rightarrow MgBr_2(c) + H_2O(liq)$, and $\Delta Hf°$ = -125.36 kcal.

Toguri et al. [102] reported $\Delta G°_{1073°K}$ = 0.267 kcal for $\frac{1}{2}MgBr_2(liq) + HCl(g) \rightarrow \frac{1}{2}MgCl_2(liq) + HBr(g)$. Using estimated thermal functions from the Dow Chemical Co. [58] we obtain $\Delta H°$ = -2.3 kcal and $\Delta Hf°$ = -121.9 kcal.

S° has been estimated as 28.0 e.u. by Kelley and King [85].

$MgBr_2$(g) Berkowitz and Marquart [49] obtained the vapor pressure by the mass spectroscopy-Knudsen effusion method. A 3rd law $\Delta H°$ from measurements at 798°K and 842°K is 49.7 kcal. The 2nd law value, at 727°K, results in $\Delta H°$ = 52.2 kcal. We have taken $\Delta H°subl$ = 51.3 kcal and $\Delta Hf°$ = -74.0 kcal.

$MgBr_2$(aq, std. state, m = 1) The values were obtained from the ions.

$MgBr_2$(aq) Lange and Streek [75] measured the heats of dilution.

$MgBr_2 \cdot 6H_2O$(c) The saturation solubility was obtained from Linke [5]; the activity and osmotic coefficients at saturation from Robinson and Stokes [6]. The resultant $\Delta G°soln$ = -7.13 kcal. We have estimated $S°$ = 95. e.u. This results in $\Delta Hf°$ = -575.9 kcal. A value of 40.7 kcal is obtained for the $\Delta H°$ for the reaction $MgBr_2 \cdot 6H_2O(c) \rightarrow MgBr_2(c) + 6H_2O(liq)$. This appears high in relation to $\Delta H°$ = 34.1 for the comparable chloride system; however, from the differential ΔH soln (obtained from the solubility measurements), which was corrected to infinite dilution we obtain $\Delta H°soln$ = -3.4 kcal and $\Delta Hf°$ = -576.2 kcal.

MgI_2(c) From Beketov's [100] measured ΔH soln in 880 H_2O, we have $\Delta Hf°$ = -87.1 kcal. Finch et al. [101] report ΔH = -35.10 kcal for the reaction of MgO(c) in excess HI (m = 0.5) to form $MgI_2 \cdot 2000\ H_2O$; and ΔH = -49.75 kcal for the solution of $MgBr_2$(c) in HI to form $MgBr_2 \cdot 9000\ H_2O$. Correcting for the concentration change, we obtain ΔH = 14.50 kcal for $MgO(c) + 2HI(aq) \rightarrow MgBr_2(c) + H_2O(liq)$ and $\Delta Hf°$ = -87.0 kcal.

Kelley and King [85] have estimated $S°$ = 31.0 e.u.

MgI_2(g) Berkowitz and Marquart [49] measured the vapor pressure by the mass spectroscopy-Knudsen effusion method. A 3rd law $\Delta H°$ from measurements at 757°K and 734°K is 45. kcal(the $\Delta(G°-H°_{298})/T$ was estimated). The 2nd law value at 640°K results in 46.4 kcal. We have taken $\Delta H°subl$ = 46 kcal from which we obtain $\Delta Hf°$ = -41 kcal.

MgI_2(aq, std. state, m = 1) The values were obtained from the ions.

$MgI_2(aq)$ The values were estimated from a consideration of the ΔHdiln of $MgCl_2$ and $MgBr_2$, and the Cl-Br-I system of the monovalent electrolytes.

$MgSO_4(c)$ The Cp° and S° were obtained from Kelley and King [85].

The following values for ΔHsoln have been obtained: Thomsen [36] -20.7 kcal (nH_2O = 420); Berthelot and Ilosvay [82] -20.8 (nH_2O = 100); Pickering [103] -20.9 and [104] -20.8 kcal (nH_2O = 420). These result in ΔHf° = -307.1, -306.8, -307.0, and -307.1 kcal, respectively.

Kelley [105] evaluated the data on the equilibrium $2MgSO_4 \rightarrow 2MgO(c) + 2SO_2(g) + O_2(g)$ and obtained ΔH° = 196.0 kcal, which leads to ΔHf° = -312.8 kcal. The results of Dewing and Richardson [106] yield ΔH° = 189.6 kcal and ΔHf° = -309.6 kcal.

From Knopf and Staude's [107] equilibrium measurements for $MgSO_4(c) \rightarrow MgO(c) + SO_3(g)$ we obtain ΔH° = 58.3 kcal and ΔHf° = -296.7 kcal.

$MgSO_4(aq, std. state, m = 1, undissociated)$ Sillen and Martell [28] list the K's and ΔH° for $Mg^{2+} + SO_4^{2-} \rightarrow MgSO_4(aq, undissoc)$. Using the measurements of Nair and Nancollas [108], ΔH° = 4.84 kcal and log K = 2.25, we obtain ΔHf° = -324.1 kcal and ΔGf° = -289.74 kcal.

$MgSO_4(aq, std. state, m = 1)$ The final values were obtained from the ions. See $Mg^{2+}(aq, std. state, m = 1)$.

$MgSO_4(aq)$ The heats of dilution were measured by Lange [109], Lange and Streeck [110], Lange and Messner [111,112], Plake [113], and Thomsen [36]. Kaganovich and Mishchenko [114] measured ΔHsoln of $MgSO_4 \cdot 7H_2O(c)$ as a function of the concentration. From Thomsen's [36] reported values for the reactions: (1) $MgCl_2(200\ H_2O) + H_2SO_4(200\ H_2O) \rightarrow MgSO_4(200\ H_2O) + 2HCl(100\ H_2O)$; (2) $MgCl_2(800\ H_2O) + H_2SO_4(400\ H_2O) \rightarrow MgSO_4(400\ H_2O) + 2HCl(400\ H_2O)$; and (3) $MgSO_4(400\ H_2O) + 2HNO_3(400\ H_2O) \rightarrow Mg(NO_3)_2(800\ H_2O) + H_2SO_4(400\ H_2O)$, we obtain (1) ΔH = -3.82 kcal, (2) ΔH = -3.76 kcal, and (3) ΔH = +3.99 kcal, which result in (1) ΔHf (200 H_2O) = -327.70, (2) ΔHf (400 H_2O) = -327.92 and (3) ΔHf (400 H_2O) =

-328.12 kcal. These are in good agreement with the values obtained from the use of the heats of diln and the ions.

$MgSO_4 \cdot H_2O$(c) The Cp° and S° were obtained from Kelley and King [85].

Thomsen [36] and Pickering [103] measured ΔH soln in 400 H_2O. Their results lead to ΔHf° = -382.5 and -384.0 kcal. Jamieson and Frost [115] reported ΔH (soln, ∞) = -14.26 kcal which results in ΔHf° = -382.9 kcal.

Kohler and Zaske [116] reported ΔH = 15.0 kcal for the decomposition to the anhydrous sulfate and H_2O(g). This results in ΔHf° = -379.9 kcal.

$MgSO_4 \cdot H_2O$(amorph) Jamieson and Frost [115] reported ΔH (soln, ∞) = -20.8 kcal; ΔHf°, then, is -376.4 kcal

Frost et al. [117] report S° = 33.0 e.u.

$MgSO_4 \cdot 2H_2O$(c) Thomsen's [36] ΔH soln in 400 H_2O is -11.4 kcal, or ΔHf° = -453.2 kcal.

Kohler and Zaske [116] reported ΔH = 25.3 kcal for the decomposition to the anhydrous salt and H_2O(g); this results in ΔHf° = -455.8 kcal.

$MgSO_4 \cdot 4H_2O$(c) Thomsen's [36] ΔH soln in 400 H_2O is -4.45 kcal or ΔHf° = -596.7 kcal.

Kohler and Zaske [116] reported ΔH = 25.8 kcal for the decomposition of the hexahydrate to the tetrahydrate and H_2O(g). ΔHf°, then, = -597.4 kcal.

$MgSO_4 \cdot 6H_2O$(c) The Cp° and S° were taken from Kelley and King [85].

Thomsen [36] reported ΔH soln in 400 H_2O to be +0.02 kcal from which we obtain ΔHf° = -737.8 kcal.

Carpenter and Jette [118], Rolla and Accame [119], Bell [120], and Kohler and Zaske [116], reported values for ΔH for decomposition of the heptahydrate to the hexahydrate and H_2O(g). Their values are 14.0, 14.6, 14.1, and 14.7 kcal, or ΔHf° = -738.1, -737.5, -738.0, and -737.5 kcal, respectively.

$MgSO_4 \cdot 7H_2O(c)$ Kaganovich and Mishchenko [114] measured ΔHsoln from m = .25 to m = 2.2. Their values at these concentrations are 3.12 and 4.54 kcal. The 21 measurements result in ΔHf° = -809.92 kcal. Kapustinskii and Samoilov [121] reported ΔHsoln = 1.82 kcal at m = .03. This results in ΔHf° = -808.20 kcal. From Perreu's [122] ΔHsoln measurements at 284°K, from nH_2O = 75 to nH_2O = 21, we obtain ΔH = 4.0 to 4.5 kcal or ΔHf° = -809.74 to -809.88 kcal. From Thomsen's [36] and Pickering's [103] ΔHsoln, 400 H_2O we have ΔH = 3.74 and 3.90 kcal or ΔHf° = -809.8 and -810.00 kcal.

From the solubility given by Linke[5] and the activities and osmotic coefficients given by Robinson and Stokes [6] we obtain ΔG°soln = 2.29 kcal and ΔGf° = -685.8 kcal. Using this value for ΔGf° and a ΔHf° = -809.92 we obtain S° = 87 e.u. which appears low. From the decomposition pressure measurements of the heptahydrate to the hexahydrate of Bell [120] we obtain ΔH° = 14.1 and ΔG° = 2.42 kcal from which we obtain S° = 89.0 e.u. Kohler and Zaske's [116] decomposition pressure is in agreement.

$Mg_3N_2(c, \alpha)$ Mitchell [123] reported the values of ΔH for the following reactions to be -287.89 kcal and -32.08 kcal, respectively.

(1) $Mg_3N_2(c) + 231.6HCl \cdot 12570\ H_2O \rightarrow 224.6HCl \cdot 3MgCl_2 \cdot 2NH_4Cl \cdot 12570\ H_2O$

(2) $2NH_3(liq) + 226.6HCl \cdot 12570\ H_2O \rightarrow 224.6HCl \cdot 3MgCl_2 \cdot 2NH_4Cl \cdot 12570\ H_2O$

Using the ΔH of Shomate and Huffman [16] for the reaction of Mg(c) in HCl(aq) and the ΔHvap of NH_3(liq), he obtains ΔH° = -88.05 kcal for $3Mg + 2NH_3(g) \rightarrow Mg_3N_2(c) + 3H_2(g)$ from which we obtain ΔHf° = -110.09 kcal.

Neumann et al. [124] reported the values of ΔH for the following to be -284.8 and -336.0 kcal, respectively.

(1) $Mg_3N_2 + 8(HCl + 20\ H_2O) \rightarrow (3MgCl_2 + 2NH_4Cl)(aq)$

(2) $3Mg(c) + 6(HCl + 20\ H_2O) \rightarrow 3MgCl_2(aq) + 3H_2(g)$

Using the ΔH = 4.14 kcal from Juza et al. [125] for the solution of NH_4Cl(c) in HCl(aq) they obtain ΔH = -42.9 kcal for $3Mg(c) + 2NH_4Cl(c) \rightarrow Mg_3N_2(c) + 2(HCl + 20\ H_2O) + 3H_2(g)$ from which ΔHf° = -114.9 kcal.

Neumann et al. [126] directly determined the value of $\Delta Hf°$ to be -116.6 kcal.

The results of Brunner are cited by Neumann et al. [124]. ΔH = -177.0 kcal for $Mg_3N_2(c)+6H_2O(c) \rightarrow 3Mg(OH)_2(ppt.) + 2NH_3(aq)$ from which we obtain $\Delta Hf°$ = -111.4 kcal. Matignon [127] and Moser and Herzner [128] measured the ΔH = -279.7 and -269.9 kcal, respectively for the reaction of Mg_3N_2 with $H_2SO_4 \cdot 200\ H_2O$. The values for $\Delta Hf°$ are -133.0 and -143.0 kcal.

Dreger [129] measured the decomposition pressure to Mg(g) and $N_2(g)$ from 1118° to 1254°K, and obtained a $\Delta H°$ apparent = 295.0 kcal, or a $\Delta Hf°$ = -189.1 kcal. Blank [130] obtained nonequilibrium values from Torsion effusion measurements in the range 1000-1250 °K of 286.3 and 218.7 kcal/mol Mg_3N_2 for the 3rd law and 2nd law values, respectively. Hildenbrand and Theard [56], in similar measurements, obtained a 2nd law non equilibrium $\Delta H°$ = 309 kcal. These values lead to $\Delta Hf°$ = -180.4, -112.8, and -203.1 kcal. Both Blank and Hildenbrand determined the condensation coefficients and corrected their vapor pressures to obtain equilibrium values. Blank's results now yield $\Delta H°$ = 242.3 kcal (3rd law) and 239.1 kcal (2nd law) and $\Delta Hf°$= -136.4 and -133.2 kcal, respectively. Hildenbrand's measurements result in an equilibrium $\Delta H°$ = 243.5 kcal and a $\Delta Hf°$ = -137.6 kcal. The latter three values are in good agreement; however, as Hildenbrand points out, there is a possibility that there is a secondary reaction going on that would interfere with the decomposition reaction. Until there is further evidence supporting this, we have selected the first mentioned $\Delta Hf°$ = -110.1 kcal.

The Dow Chemical Co. [131] tabulates the thermal functions.

$Mg(NO_3)_2(c)$ The Cp° and S° were obtained from Kelley and King [85].

Young [132] measured the ΔH's of the following reactions:

(1) $2HNO_3 \cdot 26.5\ H_2O + MgCl_2 \cdot 75.2HCl \cdot 4190\ H_2O \rightarrow$
$Mg(NO_3)_2 \cdot 77.2HCl \cdot 4216.5\ H_2O$; ΔH = 0.198 kcal

(2) $Mg(NO_3)_2 \cdot 77.2HCl \cdot 4190\ H_2O + 26.5\ H_2O(liq) \rightarrow$
$Mg(NO_3)_2 \cdot 77.2HCl \cdot 4216.5\ H_2O$; ΔH = -.113 kcal

(3) $Mg(NO_3)_2(c) + 77.2HCl \cdot 4190\ H_2O \rightarrow$

$Mg(NO_3)_2 \cdot 77.2HCl \cdot 4190\ H_2O$; $\Delta H = -20.634$ kcal

Using the reaction of Shomate and Huffman [16], $Mg(c) + 77.2HCl \cdot 4190\ H_2O \rightarrow MgCl_2 \cdot 75.2\ HCl \cdot 4190\ H_2O + H_2(g)$; $\Delta H = -111.285$ kcal, we obtain $\Delta H = -90.340$ kcal for $Mg(c) + 2HNO_3 \cdot 26.5\ H_2O \rightarrow Mg(NO_3)_2(c) + H_2(g)$ and $\Delta Hf° = -188.97$ kcal.

$Mg(NO_3)_2$(aq, std. state, m = 1) The final values were obtained from the ions. See Mg^{2+}(aq, std. state, m = 1)

$Mg(NO_3)_2$(aq) Lange and Streeck [110], Hammerschmid and Lange [133], Ewing et al. [134], and Thomsen [36] measured ΔH diln.

Pickering [135], Thomsen [36], and Ewing et al. [134] measured ΔH soln. of the hexahydrate. Their results lead to $\Delta Hf = -210.25$ kcal (400 H_2O), -210.58 kcal (400 H_2O), and -210.04 kcal (130 H_2O), respectively. Ewing also measured the ΔH soln. of the anhydrous salt, from which we obtain ΔHf(130 H_2O) = -210.20 kcal.

$Mg(NO_3)_2 \cdot 2H_2O$(c) Ewing et al. [134] measured the ΔH soln. of the anhydrous salt and that of the dihydrate. We obtain $\Delta H = -11.18$ kcal for $Mg(NO_3)_2(c) + 2H_2O(liq) \rightarrow Mg(NO_3)_2 \cdot 2H_2O(c)$ and $\Delta Hf° = -336.8$ kcal.

$Mg(NO_3)_2 \cdot 6H_2O$(c) Young [132] measured the ΔH soln. of the hexahydrate and anhydrous salt in aqueous HCl (See $Mg(NO_3)_2$(c)). The results lead to $\Delta H° = -25.729$ kcal for $Mg(NO_3)_2(c) + 6H_2O(liq) \rightarrow Mg(NO_3)_2 \cdot 6H_2O(c)$ or $\Delta Hf° = -624.59$ kcal. Similarly, from Ewing et al.'s [134] ΔH soln. in H_2O we obtain $\Delta H = -25.88$ kcal or $\Delta Hf° = -624.74$ kcal.

Lloyd et al. [136] reported decomposition pressure measurements to the anhydrous salt in the temperature range from 293°K to 333 °K. We obtain $\Delta Hf° = -618.3$ kcal.

From the solubility given by Linke [5] and the activity coefficients and osmotic coefficients given by Robinson and Stokes [6] we obtain $\Delta G°soln = -4.11$ kcal or $\Delta Gf° = -497.93$ kcal. This results in $\Delta Sf° =$

-425.3 e.u. and S° = 109.5 e.u. This appears a little high. We have estimated S° = 108 e.u. and have adjusted ΔGf° accordingly.

$MgC_2(c)$ Irmann [137] reported ΔH = -78 kcal for the reaction $MgC_2(c)$ + 180 HCl(m = 2.53, m_{NaCl} = 3.16) → $MgCl_2(aq)$ + 178 HCl(m = 2.50, m_{NaCl} = 3.16) + $C_2H_2(g)$. This results in ΔHf° = 20 kcal.

$Mg_2C_3(c)$ Irmann [137] reported ΔH = -198 kcal for the reaction $Mg_2C_3(c)$ + 360HCl (m = 2.53, m_{NaCl} = 3.16) → $2MgCl_2(aq)$ + 356HCl (m = 2.51, m_{NaCl} = 3.16) + $C_3H_4(g)$. Using ΔHf° $C_3H_4(g)$ = 44.3 kcal, we obtain ΔHf° = 17 kcal.

$MgCO_3(c)$ The Cp° and S° were obtained from Kelley and King [85]; the high temperature functions from Kelley [138].

Kapustinskii and Stakhanova [139] measured the following ΔH's:

(1) $MgCO_3(c) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(liq) + CO_2(g)$; ΔH = -12.80 kcal

(2) $MgO(c) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(liq)$; ΔH = -36.32 kcal

This results in ΔH = +23.52 kcal for $MgCO_3(c) \rightarrow CO_2(g) + MgO(c)$, or ΔHf° = -261.4 kcal.

Roth [140] reported the ΔH°decomp. = +23.6 kcal or ΔHf° = -261.5 kcal. Berthelot [141] reported ΔH = 2.7 kcal for the precipitation of $MgCO_3$ from K_2CO_3(220 H_2O) and $MgSO_4$(220 H_2O). We obtain ΔHf° = -268.1 kcal. Ellis and Mortland [142] and Foldvari-Vogl and Klibur-szky [143] obtained ΔH°decomp. from differential thermal analysis methods, to be 27.6 kcal and 27.0 kcal, respectively, or ΔHf° = -265.5 and -264.9 kcal.

We obtain from Marc and Simek's [144] vapor pressure measurements ΔH°decomp. = 28.2 kcal (3rd law) and 26.4 kcal (2nd law) or ΔHf° = -266.1 kcal and -264.3 kcal.

Langmuir [145] reviews the above data as well as the solubility measurements and the derived ΔGf° values and points out the incon-sistencies in the stability relationships in the $MgO-CO_2-H_2O$ system. We have accepted his interpretation and calculations to obtain ΔG° = 0.665 kcal for $MgCO_3 \cdot 3H_2O(c) \rightarrow MgCO_3(c) + 3H_2O(liq)$. Using our value for ΔGf° for the trihydrate = -412.6 kcal, we obtain ΔGf° = -241.9 kcal.

Mg_2Si(c) Kubaschewski and Villa [146] reported $\Delta Hf°$ = -18.6 kcal. Eremenko and Lukashenko [147], from EMF measurements obtained E(in ev) = $0.2075 - 0.77 \times 10^{-4} T$ for the range 673°K to 873°K, from which we obtain $\Delta Hf°_{773°K}$ = -19.1 kcal. This corrects to $\Delta Hf°$ = -18.7 kcal. Grjotheim et al. [148] measured the decomposition pressure in the range 1130 to 1273°K by the transpiration technique. We obtain $\Delta H°$ = 41.1 kcal/mol Mg(g) or $\Delta Hf°$ = -11.6 kcal.

From Eremenko and Lukashenko we also obtain a $\Delta Sf°(773°K)$ = -7.1 e.u. which, assuming a ΔCp = -1 cal/mol deg, corrects to $\Delta Sf°$ = -6.1 and $S°$ = 14.0 e.u. This value appears low. Mannchen and Jacobi [149] reported Cp measurements from 12°K to 300°K on $Mg_{2.12}Si$(c) and $S°$ = 19.8 cal/mol. Assuming their reported $S°$ is for $Mg_{2.12}Si$(c) we obtain $S°$ Mg_2Si(c) = 18.6 e.u. and a $\Delta Sf°$ = -1.5 e.u.

For the corresponding Ge compound ($S°_{Ge}$(c) = 7.43 e.u.) we have $S°$ = 20.7 e.u. and $\Delta Sf°$ = -2.35 e.u. In comparison with these figures we feel 18.6 e.u. is high (and -1.5 e.u. too positive). We have therefore adjusted $S°$ to = 18.0 e.u.

$MgSiO_3$(c) Furukawa and Reilly [150] evaluated the low temperature Cp and high temperature heat content and have tabulated the thermal functions up to 2000°K.

Torgeson and Sahama [34] by HF soln. calorimetry of $Mg(OH)_2$(c), SiO_2(c, quartz), and $MgSiO_3$(c) obtained ΔH = 0.16 kcal for $Mg(OH)_2$(c) + SiO_2(c) → $MgSiO_3$(c) + H_2O(liq). This results in $\Delta Hf°$ = -370.22 kcal.

Henderson and Taylor [151] reported $\Delta G°_{1823°K}$ = -5.1 kcal for the formation from the oxides. This results in $\Delta Hf°$ = -368.5 kcal.

Mg_2SiO_4(c) Furukawa and Reilly [150] tabulated the thermal functions up to 2000°K.

Torgeson and Sahama [34] by HF soln. calorimetry of $Mg(OH)_2$(c), SiO_2(c, quartz), and Mg_2SiO_4(c) obtained ΔH = 2.58 kcal for $2Mg(OH)_2$(c) + SiO_2(c) → Mg_2SiO_4(c) + $2H_2O$(liq), from which we obtain $\Delta Hf°$ = -520.45 kcal.

King et al. [152] from HF soln. calorimetry obtained $\Delta H°$ = -13.86 kcal for $2MgO(c) + SiO_2(c) \rightarrow Mg_2SiO_4(c)$ which leads to $\Delta Hf°$ = -519.20 kcal. Henderson and Taylor [151] reported $\Delta G°_{1823°K}$ = -9.4 kcal for the formation of $Mg_2SiO_4(c)$ from the oxides. This results in $\Delta Hf°$ = -515.4 kcal.

$Mg_3Si_2O_5(OH)_4(c)$ King et al. [152] from HF soln. calorimetry obtained $\Delta H°$ = -39.86 kcal for $3MgO(c) + 2SiO_2(c) + 2H_2O(liq) \rightarrow Mg_3Si_2O_5(OH)_4(c)$ from which we obtain $\Delta Hf°$ = -1043.4 kcal.

The Cp° and S° were also obtained from King et al.

$Mg_3Si_4O_{10}(OH)_2(c)$ Barany [153] from HF soln. calorimetry obtained $\Delta H°$ = -44.9 kcal for $3MgO(c) + 4SiO_2(c) + H_2O(liq) \rightarrow Mg_3Si_4O_{10}(OH)_2(c)$ from which we obtain $\Delta Hf°$ = -1415.5 kcal.

The Cp° and S° were obtained from Robie and Stout [154].

$MgB_{12}(c)$ The thermal functions were obtained from Germaidze et al. [155] who also measured the Mg(g) pressure over the MgB_{12} to be 10^{-5} atm. at 1700°K. This results in $\Delta Hf°$ = -53.4 kcal.

$MgAl_2O_4(c)$ The Dow Chemical Co. [156] tabulated the thermal functions.

Navrotsky and Kleppa [157] measured the ΔH soln. of MgO(c), Al_2O_3 (c, α) and $MgAl_2O_4(c)$ in $9PbO \cdot 3CdO \cdot 4B_2O_3$ (melt) and obtained $\Delta H_{970°K}$ = -8.72 kcal for the formation from the component oxides. This results in $\Delta H°$ = -8.6 kcal and $\Delta Hf°$ = -552.9 kcal.

Altman [20] from Knudsen effusion decomposition pressure measurements [$MgAl_2O_4(c) \rightarrow Mg(g) + \frac{1}{2}O_2(g) + Al_2O_3(c)$], supports a $\Delta H°$ = -5 kcal for the formation from the oxides. Altman [158] from transpiration experiments on the Al-MgO and Al-$MgAl_2O_4$ systems obtained $\Delta H°$ = -7 kcal. Grjotheim et al. [159], by the transpiration method, measured the K's for $4MgO(c) + 2Al(liq) \rightarrow MgAl_2O_4(c) + 3Mg(g)$. They considered the system ideal. On this basis we obtain $\Delta H°$ = 7.3 kcal (2nd law) and -7.6 kcal (3rd law). Altman [20] corrects their results for the activity

of Al. Using the thermal functions mentioned above we obtain a 3rd law ΔH° = -8.2 kcal and ΔHf° = -552.5 kcal. Grjotheim et al. [160] repeat their measurements and obtain a ΔH° = +1.1 kcal. In a later series of measurements on the Al-Mg-SiO system they [161] obtain the activity of Al and pressure of Mg(g) for the equilibrium process, $4MgO(c) + 2AlSi(liq) \rightarrow MgAl_2O_4(c) + 3Mg(g)$. This results in ΔH° = -7.4 kcal for formation from the oxides and ΔHf° = -551.7 kcal. In a reaction involving MgO(c) and $Al_4C_3(c)$ they [162] obtain ΔH° = -11.1 kcal and ΔHf° = -555.4 kcal. Rao and Dadape [163] measured the K's of the reaction, $4MgO(c) + 3AlCl(g) \rightleftarrows MgAl_2O_4(c) + AlCl_3(g) + 3Mg(g)$ in the range 1298°K to 1465°K. We obtain ΔHf° = -554.0 kcal (3rd law) and a ΔH° = -9.7 kcal for formation from the oxides and ΔHf° = -554.7 kcal (2nd law) and a ΔH° = -10.4 kcal.

Zaionchovskii and Rubal'skaya [164] reported ΔHf° = -567.1 kcal.

The first mentioned ΔHf° was selected.

$Mg_2Al_4Si_5O_{18}(c)$ The Cp° and S° were obtained from Weller and King [165]; the high temperature heat content from Pankratz and Kelley [166].

Henderson and Taylor [151] reported $\Delta G^\circ_{1733°K}$ = -12.5 kcal for $2MgO(c) + 2Al_2O_3(c) + 5SiO_2(c) \rightarrow Mg_2Al_4Si_5O_{18}(c)$ from which we obtain ΔHf° = - 2177. kcal.

BIBLIOGRAPHY

1. D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. Bailey, and R. Schumm, Selected values of chemical thermodynamic properties, Natl. Bur. Standards Technical Note 270-3, 264 pp (U. S. Govt. Printing Office, Jan. 1968).

2. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, Selected values of thermodynamic properties of metals and alloys, 963 pp (John Wiley and Sons, Inc. 1963).

3. R. Hultgren, R. L. Orr, and K. K. Kelley, Supplement to Selected values of thermodynamic properties of metals and alloys; Mg, Oct. 1966.

4. C. E. Moore, Atomic energy levels, Vol. 1 and 3, Natl. Bur. Standards Circ. 467, (U.S. Govt. Printing Office, 1949-1958).

5. W. F. Linke, Solubilities of inorganic and metal organic compounds, Vol. II, 4th edition, (American Chemical Society, Wash., D. C., 1965).

6. R. A. Robinson and R. H. Stokes, Electrolyte Solutions, 2nd edition, 559 pp , (Academic Press, Inc. New York, 1959).

7. Dow Chemical Company - JANAF Thermochemical Tables, Dec. 31, 1965.

8. G. T. Furukawa, M. L. Reilly, J. M. Henning, T. B. Douglas, A. C. Victor, and A. R. Beaudoin, Natl. Bur. Standards Report 6484, p. 17 and table 2 - 10 (1959).

9. W. Muthmann and L. Weiss, Ann. 331, 1 (1904).

10. J. E. Moose and S. W. Parr, J. Am. Chem. Soc. 46, 2656 (1924).

11. H. von Wartenburg, Z. Elektrochem. 15, 866 (1909).

12. F. J. Rogers, Am. J. Sci. 143, 301 (1892).

13. A. F. Vorob'ev and S. M. Skuratov, Zhur. Fiz. Khim. 32, 2580 (1958).

14. S. A. Shchukarev, I. V. Vasil'kova, and B.N. Sharupin, Vestnik Leningrad. Univ. 15, No. 10, Ser. Fiz. i Khim. No. 2, 112 (1960).

15. C. E. Holley and E. J. Huber, J. Am. Chem. Soc. 73, 5577 (1951).

16. C. H. Shomate and E. H. Huffman, J. Am. Chem. Soc. 65, 1625 (1943).

17. W. F. Giauque, J. Am. Chem. Soc. 71, 3192 (1949).

18. L. Brewer and R. F. Porter, J. Chem. Phys. 22, 1867 (1954).

19. C. A. Alexander, J. S. Ogden, and A. Levy, J. Chem. Phys. 39, 3057 (1963).

20. R. L. Altman, J. Phys. Chem. 67, 366-369 (1963).

21. R. F. Porter, W. A. Chupka, and M. G. Inghram, J. Chem. Phys. 23, 1347 (1955).

22. E. Bulewicz and T. Sugden, Trans. Faraday Soc. 55, 720 (1959).

23. I. Veits, L. Gurvitch, N. P. Rtishcheva, Zhur. Fiz. Khim. 32, 2532 (1958).

24. J. Drowart, G. Exsteen, and G. Verhaegen, Trans. Faraday Soc. 60, 1920 (1964).

25. L. Brewer and S. Trajmar, J. Chem. Phys. 36, 1585 (1962).

26. Dow Chemical Company - JANAF Thermochemical Tables, Sept. 30, 1963.

27. V. I. Pepekin, T. N. Dymova, Yu. A. Libeder, and A. Yu. Apin, Zhur. Fiz. Khim. 38, 1024 (1964).

28. L. G. Sillen and A. E. Martell, Stability constants of metal-ion complexes, Soc. London, Spec. Publ. No. 17, 754 pp (London 1964).

29. P. B. Hostetler, Am. J. Sci. 261, 238 (1963).

30. Dow Chemical Company - JANAF Thermochemical Tables, Mar. 31, 1967.

31. L. S. Wells and K. Taylor, J. Research Natl. Bur. Standards 19, 215 (1937).

32. K. Taylor and L. S. Wells, J. Research Natl. Bur. Standards, 21, 133 (1938).

33. W. F. Giauque and R. C. Archibald, J. Am. Chem. Soc. 59, 561 (1937).

34. D. R. Torgeson and T. G. Sahama, J. Am. Chem. Soc. 70, 2156 (1948).

35. W. A. Roth and P. Chall, Z. Elektrochem. 34, 185 (1928).

36. J. Thomsen, Thermochemische untersuchungen, Vols. I, II, III, and IV, (J. A. Barth, Leipzig, 1882-1886).

37. M. Berthelot, Ann. chim. et phys. (6) 11, 310 (1887).

38. T. C. Ehlert, G. D. Blue, J. W. Green, and J. L. Margrave, J. Chem. Phys. 41, 2250 (1964).

39. A. G. Gaydon, Dissociation energies and spectra of diatomic molecules (Chapman and Hall, Ltd., London, 1953).

40. G. Herzberg, Molecular spectra and molecular structure. I. Spectra of diatomic molecules, 2nd ed., (D. Van Nostrand Company, New York, 1950).

41. Dow Chemical Company - JANAF Thermochemical Tables, Mar. 31, 1966.

42. E. Rudzitis, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. 68, 2978 (1964).

43. P. Gross, C. Hayman, and D. L. Levi, Trans. Faraday Soc. 50, 477 (1954).

44. A. F. Kapustinskii and K. K. Samplavskaya, Zhur. Neorg. Khim. 6, 2237 (1961).

45. A. Guntz, Ann. chim. et phys. (6) 3, 39 (1884).

46. A. Guntz, Compt. rend. 98, 819 (1884).

47. H. von Wartenberg, Z. anorg. u. allgem. Chem. 249, 100 (1942).

48. E. Petersen, Z. physik. Chem. 4, 384 (1889).

49. J. Berkowitz and J. R. Marquart, J. Chem. Phys. 37, 1853 (1962).

50. J. W. Green, G. D. Blue, T. C. Ehlert, and J. L. Margrave, J. Chem. Phys. 41, 2245 (1964).

51. R. R. Hammer and J. A. Pask, J. Am. Ceram. Soc. 47, 264 (1964).

52. M. A. Greenbaum, H. C. Ko, M. Wong, and M. Farber, J. Phys. Chem. 68, 965 (1964).

53. J. L. Margrave, CPIA Publication No. 54U I 43 (Aug. 1964).

54. L. Le Boucher, Anales soc. espãn. fis. y quim. 32, 1142 (1934).

55. D. L. Hildenbrand, W. F. Hall, F. Ju, and N. D. Potter, J. Chem. Phys. 40, 2882 (1964).

56. D. L. Hildenbrand and L. P. Theard, U. S. Dept. Comm. Office Tech. Serv. AD 258, 410 24 pp (1961).

57. K. G. Gunther, Glastech. Ber. 31, 9 (1958).

58. Dow Chemical Company - JANAF Thermochemical Tables, June 30, 1966.

59. H. Bommer and E. Hohmann, Z. anorg. u. allgem. Chem. 248, 357 (1941).

60. K. Sanò, Nippon Kagaku Zasshi, 57, 1019 (1936).

61. W. D. Treadwell, Schweiz Arch. angew. Wiss. u. Tech. 6, 69 (1940).

62. W. D. Treadwell and A. Cohen, Helv. Chim. Acta 22, 433 (1939).

63. K. Sano, Kinzoku - no-Kenkyu 12, 247 (1935).

64. R. Tsuchiya, Sci. Repts Tohoku Imp. Univ. (I) 37, 9 (1953).

65. I. L. Reznikov, Zhur. Priklad. Khim. 23, 897 (1950).

66. J. J. Egan, W. McCoy and J. Bracker, Symp. thermodyn. Nucl. Mtls., Vienna 1962, 14 pp.

67. W. D. Treadwell, A. Ammann, and T. Zurrer, Helv. Chim. Acta 19, 1255 (1936).

68. B. F. Markov, Yu. K. Delimarskii, and I. D. Panchenko, Zhur. Fiz. Khim. 29, 51 (1955).

69. R. Lorenz and H. Velde, Z. anorg. u allgem. Chem. 183, 81 (1929).

70. M. Takahashi, J. Elektrochem. Soc. Japan, Overseas Ed. 29, E54 (1961).

71. E. E. Schrier and H. M. Clark, J. Phys. Chem. 67, 1259 (1963).

72. B. N. Kushkin, V. V. Rodyakin, and S. I. Kuznetsov, Zhur. Neorg. Khim. 12, 791 (1967).

73. W. Fischer, T. Petzel, and S. Lauter, Z. anorg. u. allgem. Chem. 333, 226 (1964).

74. C. G. Maier, U. S. Bur. Mines, Tech. Papers 360 54 pp. (1925).

75. E. Lange and H. Streeck, Z. physik. Chem. A152, 1 (1931).

76. A. B. Zdanovskii and L. D. Deryabina, Zhur. Fiz. Khim. 39, 678 (1965).

77. R. Fricke, Z. Elektrochem. 35, 361 (1929).

78. K. P. Mishchenko and I. F. Yakovlev, Zhur. Obshchei. Khim. 29, 1761 (1959).

79. O. Ya. Samoilov, Izvest. Akad. nauk S.S.S.R., Otdel. Khim Nauk 1952, 627; Doklady Akad. Nauk S.S.S.R. 81, 641 (1951).

80. N. K. Voskresenskaya and K. S. Ponomareva, Zhur. Fiz. Khim. 20, 433 (1946).

81. L. T. Richardson and R. C. Wells, J. Wash. Acad. Sci. 21, 243 (1931).

82. M. Berthelot and L. Ilosvay, Ann. chim. et phys. (5) 29, 295 (1883).

83. K. P. Mishchenko, I. L. Reznikov, M. L. Klyueva, V. V. Sokolov, and Yu. A. Polyakov, Zhur. Priklad. Khim. 38, 1939 (1965).

84. T. W. Richards, A. W. Rowe, and L. L. Burgess, J. Am. Chem. Soc. 32, 1176 (1910).

85. K. K. Kelley and E. G. King, Contributions to the data on theoretical metallurgy. XIV. Entropies of the elements and inorganic compounds, U. S. Bur. Mines, Bull. 592, 149 pp (1961).

86. A. E. Auzhbikovich, Zhur. Priklad. Khim. 12, 1595 (1939).

87. H. V. Kondirev and G. V. Berezovskii, Zhur. Obshchei Khim. 5, 1246 (1935).

88. I. H. Derby and V. Yngve, J. Am. Chem. Soc. 38, 1439 (1916).

89. K. Sano, Sci. Repts. Tohoku Univ. (1) 25, 184 (1936).

90. K. Sano, Nippon Kagaku Zasshi, 59, 1145 (1938).

91. A. F. Vorob'ev, N. M. Privalova, A. S. Monaenkova, and S. M. Skuratov, Doklady Akad. Nauk S.S.S.R. 135, 1388 (1960).

92. S. Drakin and Ch. Yu. Chzhan, Zhur. Fiz. Khim. 38, 2800 (1964).

93. C. Smeets, Natuurw. Tijdschr. (Ghent) 15, 105 (1933).

94. G. F. Smith, O. W. Rees, and V. R. Hardy, J. Am. Chem. Soc. 54, 3513 (1932).

95. H. S. Jongenburger and R. H. Wood, J. Phys. Chem. 69, 4231 (1965).

96. T. A. Nosova, Zhur. Neorg. Khim. 11, 1970 (1966).

97. K. K. Kelley, U. S. Bur.Mines, Tech. Papers 676, 26 pp (1945).

98. E. I. Savinkova and T. A. Degtyareva, Izvest. Vysshikh Ucheb. Zavedenii, Khim. i Khim. Technol. 5, 292 (1962).

99. Ya. E. Vel'nyanskii and E. I. Savinkova, Zhur. Priklad. Khim. 26, 808 (1953).

100. N. Beketov, Bull. acad. imp. sci. (St. Petersbourg) 34, 291 (1892).

101. A. Finch, P. J. Gardner, and C. J. Steadman, Private Communication, 1967.

102. J. Toguri, H. Flood, and T. Forland, Acta Chem. Scand. 17, 1502 (1963).

103. S. U. Pickering, J. Chem. Soc. 47, 100 (1885).

104. S. U. Pickering, J. Chem. Soc. 51, 290 (1887).

105. K. K. Kelley, Contributions to the data on theoretical metallurgy. VII The thermodynamic properties of sulfur and its inorganic compounds, U. S. Bur. Mines, Bull. 406, 154 pp. (1937).

106. E. W. Dewing and F. D. Richardson, Trans. Faraday Soc. 55, 611 (1959).

107. H. J. Knopf and H. Staude, Z. physik. Chem. 204, 265 (1955).

108. V. S. K. Nair and G. H. Nancollas, J. Chem. Soc. 1958, 3706.

109. E. Lange, Fortschr. Chem., Physik u. physik. Chem. 19, No. 6 (1928).

110. E. Lange and H. Streeck, Z. physik. Chem. A157, 1 (1931).

111. E. Lange and G. Messner, Z. Elektrochem. 33, 431 (1927).

112. E. Lange and G. Messner, Naturwiss. 15, 521 (1927).

113. E. Plake, Z. physik. Chem. A162, 257 (1932).

114. Yu. Ya. Kaganovich and K. P. Mishchenko, Zhur. Obshchei Khim. 21, 28 (1951).

115. J. W. S. Jamieson and G. B. Frost, Can. J. Chem. 34, 583 (1956).

116. K. Kohler and P. Zäske, Z. anorg. u. allgem. Chem. 331, 1 (1964).

117. G. B. Frost, W. G. Breck, R. N. Clayton, A. H. Reddoch, and C. G. Miller, Can. J. Chem. 35, 1446 (1957).

118. C. D. Carpenter and E. R. Jette, J. Am. Chem. Soc. 45, 578 (1923).

119. L. Rolla and L. Accame, Atti accad. nazl. Lincei Rend., Classe sci. fis., mat. e nat. (5) 22II, 109 (1913).

120. J. Bell, J. Chem. Soc. 1940, 72.

121. A. F. Kapustinskii and O. Ya. Samoilov, Zhur. Fiz. Khim. 26, 918 (1952).

122. J. Perreu, Compt. rend. 190, 429 (1930).

123. D. W. Mitchell, Ind. Eng. Chem. 41, 2027 (1949).

124. B. Neumann, C. Kröger, H. Kunz, Z. anorg. u. allgem. Chem. 207, 133 (1932).

125. R. Juza, K. Fasold, C. Haeberle, Z. anorg. u. allgem. Chem. 234, 75 (1937).

126. B. Neumann, C. Kröger, and H. Haebler, Z. anorg. u. allgem. Chem. 204, 81 (1932).

127. C. Matignon, Compt. rend. 154, 1351 (1912).

128. L. Moser and R. Herzner, Monatsh. 44, 115 (1923).

129. L. H. Dreger, Ph.D. thesis, Univ. Wisconsin, microfilm # 62-1960.

130. B. A. Blank, UCRL 16018, 45 pp (1965).

131. Dow Chemical Company - JANAF Thermochemical Tables, Dec. 31, 1960.

132. F. E. Young, J. Am. Chem. Soc. 66, 773 (1944).

133. H. Hammerschmid and E. Lange, Z. physik. Chem. A160, 445 (1932).

134. W. W. Ewing, E. Klinger, and J. D. Brandner, J. Am. Chem. Soc. 56, 1053 (1934).

135. S. U. Pickering, J. Chem. Soc. 53, 865 (1888).

136. E. Lloyd, C. B. Brown, D. G. R. Bonnell, and W. J. Jones, J. Chem. Soc. 1928, 658.

137. F. Irmann, Helv. Chim. Acta 31, 1584 (1948).

138. K. K. Kelley, Contributions to the data on theoretical metallurgy. XIII. High temperature heat content, heat-capacity, and entropy data for the elements and inorganic compounds, U. S. Bur. Mines, Bull. 584, 232 pp (1960).

139. A. F. Kapustinskiĭ and M. S. Stakhanova, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1954, 587.

140. W. A. Roth, J. prakt. Chem. (2) 158, 117 (1941).

141. M. Berthelot, Ann. chim. et phys. (5) 4, 160 (1875).

142. B. G. Ellis and M. M. Mortland, Am. Mineralogist, 47, 371 (1962).

143. M. Foldvári-Vogl and B. Kliburszky, Acta Geol. Acad. Sci. Hung. 5, 187 (1958).

144. R. Marc and A. Simek, Z. anorg. Chem. 82, 17 (1913).

145. D. Langmuir, J. Geol. 73, 730 (1965).

146. O. Kubaschewski and H. Villa, Z. Elektrochem. 53, 32 (1949).

147. V. N. Eremenko and G. M. Lukashenko, Symp. thermodyn. Nuclear Mtls, Vienna 1965, Paper SM 66/87, 26 pp.

148. K. Grjotheim, O. Herstad, S. Petrucci, R. Skarbo, and J. Toguri, Rev. chim. Acad. Rep. Populaire Roumaine 7, 217 (1962).

149. W. Mannchen and G. Jacobi, Z. Naturforsch. 20b, 178 (1965).

150. G. Furukawa and M. L. Reilly, Natl. Bur. Standards Rept. 7587, pp 94, 146, and 148.

151. D. Henderson and J. Taylor, J. Iron Steel Inst. (London) 204, 39 (1966).

152. E. G. King, R. Barany, W. W. Weller, and L. B. Pankratz, U. S. Bur. Mines Rept. Invest. 6962 19 pp (1967).

153. R. Barany, U. S. Bur. Mines Rept. Invest. 6251, 9 pp (1963).

154. R. A. Robie and J. W. Stout, J. Phys. Chem. 67, 2252 (1963).

155. M. S. Germaidze, P. V. Geld, and S. M. Letun, Zhur. Prikladnoi Khim. 39, 1941 (1966).

156. Dow Chemical Company - JANAF Thermochemical Tables, Mar. 31, 1963.

157. A. Navrotsky and O. J. Kleppa, Inorg. Chem. 5, 192 (1966).

158. R. L. Altman, J. Phys. Chem. 68, 3425 (1964).

159. K. Grjotheim, O. Herstad, and J. M. Toguri, Can. J. Chem. 39, 443 (1961).

160. K. Grjotheim, O. Herstad, and J. M. Toguri, Trans. Can. Inst. Mining Met. 65, 221 (1962).

161. K. Grjotheim, O. Herstad, P. Skarbö and J. M. Toguri, Can. J. Chem. 41, 739 (1963).

162. K. Grjotheim, O. Herstad, and K. S. Johannessen, Z. anorg. u. allgem. Chem. 328, 267 (1964).

163. D. Rao and V. V. Dadape, J. Phys. Chem. 71, 537 (1967).

164. Ya. A. Zaionchovskii and E. V. Rubal'skaya, Izvest. Akad. Nauk S.S.S.R. Neorg. Materially 1, 1376 (1965).

165. W. W. Weller and E. G. King, U. S. Bur. Mines Rept. Invest. 6343, 7 pp (1963).

166. L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines Rept. Invest. 6555, 7 pp (1964).

Table III

Selected Values for Some Mg Compounds at 298°K

Compound	State	ΔHf° kcal/mole	ΔGf° kcal/mole	S° cal/deg mol
Mg	c	0	0	7.81
Mg	g	35.30	27.04	35.502
Mg^+	g	213.100		
Mg^{2+}	g	561.299		
Mg^{2+}	aq std. state, m = 1	-111.58	-108.7	-33.0
MgO	macro crystal (periclase)	-143.81	-136.10	6.44
MgO	micro crystal	-142.92	-135.27	6.67
MgO	g	4.		
MgH_2	c	-18.0	-8.6	7.43
$MgOH^+$	aq std. state, m = 1		-149.8	
$Mg(OH)_2$	c	-220.97	-199.23	15.10
$Mg(OH)_2$	ppt	-220.0		
$Mg(OH)_2$	aq std. state, m = 1	-221.52	-183.9	-35.6
$Mg(OH)_2$	g	-134		
MgF	g	-53.0	-59.2	52.79
MgF_2	c	-268.5	-255.8	13.68
MgF_2	g	-173.0	-174.6	61.73
MgCl	g	-10.	-16.	55.8
$MgCl_2$	c	-153.28	-141.45	21.42
$MgCl_2$	g	-95.7		
$MgCl_2$	aq std. state, m = 1	-191.48	-171.4	-6.0
	50 H_2O	-190.23		
	100 H_2O	-190.59		
	400 H_2O	-190.94		
	1,000 H_2O	-191.080		
	5,000 H_2O	-191.269		
	10,000 H_2O	-191.323		
	∞ H_2O	-191.48		

Compound	State	ΔHf° kcal/mole	ΔGf° kcal/mole	S° cal/deg mol
$MgCl_2 \cdot H_2O$	c	-231.03	-205.98	32.8
$MgCl_2 \cdot 2H_2O$	c	-305.86	-267.24	43.0
$MgCl_2 \cdot 4H_2O$	c	-453.87	-388.03	63.1
$MgCl_2 \cdot 6H_2O$	c	-597.28	-505.49	87.5
$Mg(ClO_4)_2$	c	-135.97		
$Mg(ClO_4)_2$	aq std. state, m = 1	-173.40	-112.8	54.0
$Mg(ClO_4)_2 \cdot 6H_2O$	c	-584.5	-445.3	124.5
MgOHCl	c	-191.1	-174.9	20.0
$MgBr_2$	c	-125.3	-120.4	28.0
$MgBr_2$	g	-74.0		
$MgBr_2$	aq std. state, m = 1	-169.68	-158.4	6.4
	100 H_2O	-168.98		
	400 H_2O	-169.18		
	1,000 H_2O	-169.304		
	5,000 H_2O	-169.476		
	10,000 H_2O	-169.528		
	∞ H_2O	-169.68		
$MgBr_2 \cdot 6H_2O$	c	-576.0	-491.4	95
MgI_2	c	-87.0	-85.6	31.0
MgI_2	g	-41		
MgI_2	aq std. state, m = 1	-137.96	-133.4	20.2
	400 H_2O	-137.49		
	1,000 H_2O	-137.59		
	∞ H_2O	-137.96		
$MgSO_4$	c	-307.1	-279.8	21.9
$MgSO_4$	aq., std. state m = 1, undissoc	-324.1	-289.74	-1.7

Compound	State	ΔHf° kcal/mole	ΔGf° kcal/mole	S° cal/deg mol
$MgSO_4$	aq			
	std. state, m = 1	-328.90	-286.7	-28.2
	50 H_2O	-327.41		
	100 H_2O	-327.59		
	400 H_2O	-327.88		
	1,000 H_2O	-328.08		
	5,000 H_2O	-328.358		
	10,000 H_2O	-328.467		
	∞ H_2O	-328.90		
$MgSO_4 \cdot H_2O$	c	-382.9	-341.5	30.2
$MgSO_4 \cdot H_2O$	amorph	-376.4	-335.8	33.0
$MgSO_4 \cdot 2H_2O$	c	-453.2		
$MgSO_4 \cdot 4H_2O$	c	-596.7		
$MgSO_4 \cdot 6H_2O$	c	-737.8	-629.1	83.2
$MgSO_4 \cdot 7H_2O$	c	-809.92	-686.4	89.
Mg_3N_2	c	-110.1		
$Mg(NO_3)_2$	c	-188.97	-140.9	39.2
$Mg(NO_3)_2$	aq			
	std. state, m = 1	-210.70	-161.9	37.0
	50 H_2O	-210.14		
	100 H_2O	-210.16		
	400 H_2O	-210.28		
	1,000 H_2O	-210.364		
	5,000 H_2O	-210.502		
	10,000 H_2O	-210.551		
	∞ H_2O	-210.70		
$Mg(NO_3)_2 \cdot 6H_2O$	c	-624.59	-497.3	108
MgC_2	c	20		
Mg_2C_3	c	17		
$MgCO_3$	c, magnesite	-261.9	-241.9	15.7

Compound	State	ΔHf° kcal/mole	ΔGf° kcal/mole	S° cal/deg mol
Mg_2Si	c	-18.6	-18.0	18.
$MgSiO_3$	c, clinoenstatite	-370.22	-349.46	16.19
Mg_2SiO_4	c, forsterite	-519.6	-491.2	22.74
$Mg_3Si_2O_5(OH)_4$	c, chrysotile	-1043.4	-965.1	52.9
$Mg_3Si_4O_{10}(OH)_2$	c, talc	-1415.5	-1324.8	62.3
MgB_{12}	c	-53.	-52.	21.4
$MgO \cdot Al_2O_3$	c	-552.9	-523.1	19.27
$Mg_2Al_4Si_5O_{18}$	c, cordierite	-2177	-2055	97.3

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13. ABSTRACT This report presents the results and interpretation of five recent NBS experimental studies of thermodynamic properties, two reviews which refine data treatment and evaluation, and one new critical assessment of published heats of formation. The heat capacity of beryllium nitride, Be_3N_2, was precisely measured from 0 to 315 K; after judicious correction for the irreducible impurities, the data led to the common thermodynamic properties from 0 to 315 K, complementing earlier NBS measurements from 273 to 1173 K. Precise high-temperature calorimetry gave the heat capacity of tungsten from 1100 to 2600 K (showing no detectable difference between two samples, one triple-zone-refined and 99.999% pure); finally corrected results are given also for solid and liquid beryllium aluminate, $BaAl_2O_4$, from 1200 to 2400 K. A mass-spectrometric investigation of Al_2O_3 containing 5.8% BeO identified the high-temperature gas species and gave values for their standard heats of formation. As part of the current NBS microwave and infrared infrared investigation of the alkali-hydroxide molecules, the high-temperature microwave spectra of four isotopic varieties of RbOH were observed and analyzed to give their molecular constants like CsOH (studied earlier), RbOH is linear, with a low-frequency bending vibration of large amplitude. Two reviews deal with reaction calorimetry involving fluorine compounds: One documents the inadequacy of estimation rules for unmeasured inorganic fluorides and recommends a systematic cataloging of results to achieve better consistency; while the other describes a new computer subroutine for the automatic reduction of bomb-calorimetry data on organic fluorine compounds. As the result of an up-to-date critical evaluation of the published data giving ΔHf°_{298}, ΔGf°_{298}, and S°_{298} of magnesium compounds, values are documented and tabulated for 60 species of interest in "light-element" applications.

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